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16. ABSTRACT

The report describes an initial source assessment environmental test plan, developed to investigate the fate of various constituents during coal gasification. The plan is an approach to the problems associated with sampling point selection, sample collection, and sample analysis which is based on a HYGAS-type process. The report includes a general process description, process steps, effects of operating conditions, sampling, analytical methods, and significance of results. In order to be implemented, this environmental test plan would have to be integrated into the operating program of a specific facility. Although this integration has not taken place, it would be a next step toward data acquisition.

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INITIAL ENVIRONMENTAL TEST PLAN FOR SOURCE ASSESSMENT OF COAL GASIFICATION

by

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Prepared for

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ABSTRACT

This research effort has been directed toward the systematic development of an environmental test plan to investigate the fate of a large number of constituents and certain potential pollutants of coal during gasification. The test plan is a logical and well-conceived approach to the problems associated with sampling point selection, sample collection, and sample analysis for a complex and much needed process.

In accordance with the tasks outlined in the project proposal, the test plan comprises 6 major sections.

The first contains a process flow sheet of a possible HYGAS-based coal gasification installation. Accompanying this flow sheet are three examples of material balances calculated for a bituminous, subbituminous, and a lignite coal.

The second section contains the estimated material balances for 38 constituent elements as they might be distributed during gasification in a typical commercial plant. Extensive thermodynamic calculations based on chemical analyses have been performed in the development of these material balances. Supporting discussions and the results of thermodynamic calculations are included in the appendixes.

The third report section assesses the effects of possible process upsets on the distribution of the elements. A wide range of process operating conditions as evaluated by computer simulation indicate that moderate variations in temperature and major variations in pressure do not significantly change the expected trace-element distribution.

In the fourth section, HYGAS pilot plant sampling locations are described as well as methods of high pressure-high temperature gas, solid, and liquid sampling.

The fifth section contains a list of suggested analytical methods to be used in an actual testing program in support of a comprehensive environmental study of coal gasification processes.

The last section discusses the significance of the results of the analytical methods as proposed herein.

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HYGAS PROCESS DESCRIPTION

Introduction

This study was initiated by the Environmental Protection Agency to investigate the fate of trace elements of coal during the gasification process for production of high-Btu pipeline-quality gas. The ultimate goal of the investigation is to provide information that will enable the environmentally sound operation of future commercial-scale coal-gasification plants.

In order to attain this goal, a test plan has been developed which provides an estimated environmental impact of three examples of HYGAS-based coal-gasification facilities.

The test plan follows a logical program of investigation, which includes examples of HYGAS process designs, followed by engineering estimates and calculations (based on actual analytical data) of the possible distribution of trace elements during gasification. Next, the test plan is oriented toward the HYGAS pilot plant where a sampling program could be undertaken for solid, liquid, and gaseous process streams. The suggested analyses of pilot plant samples for trace elements and other species will provide important data on the high Btu-coal gasification processes and serve to refine the distribution estimates which are presented in this report.

Instrumental to the successful completion of this test plan, was analytical data obtained from the analysis of four series of coal feed, and residue samples for the determination of 38 minor and trace elements.

The samples consisted of feed and solid residues of two separate hydrogasification runs on Montana lignite plus the feed and solid residues of two series of pretreatment and hydrogasification runs on Illinois No. 6 bituminous coal, but included no gaseous or liquid samples.

Figure 1 is a block-flow diagram of a HYGAS-based, large coal-gasification plant with an integrated steam-oxygen gasifier. This flow sheet, and the related material balances, depict only one of many possible variations in the design of coal gasification facilities based on the HYGAS process. The final process design for any gasification plant will logically depend upon many factors including the particular coal feed, the plant location, the engineering contractor, and the plant owner, among others. This particular plant design is sized to produce 3.0528 GJ/s (250 billion Btu/day)* of synthetic natural gas (SNG). The flow diagram shows details for a minimum discharge system in which all process water is recycled to the process after water treatment, and most gaseous effluents are treated to reduce pollutant concentrations to acceptable levels. For example, the concentration of sulfur dioxide (SO_2) in the steam-plant stack-gas is reduced to 5.159 kg per 10 GJ of energy produced (1.2 lb SO_2/million Btu). Measurements of trace-element levels in the by-product streams will provide valuable data on recovery efficiencies for each process, on potential environmental problems, and on the salability of each particular by-product. In accordance with this test plan, the SNG product stream should be analyzed for all trace elements; however, it is expected that extremely low levels of volatile trace elements will be present, whereas nonvolatile elements will be undetectable.

Tables 1 through 3 describe quantitatively the solid, liquid, and gaseous streams for process designs based on bituminous, subbituminous, and lignite coal feeds. The first part of each table details the compositions of the gaseous and liquid streams; the second part describes the solid and by-product streams from the process.

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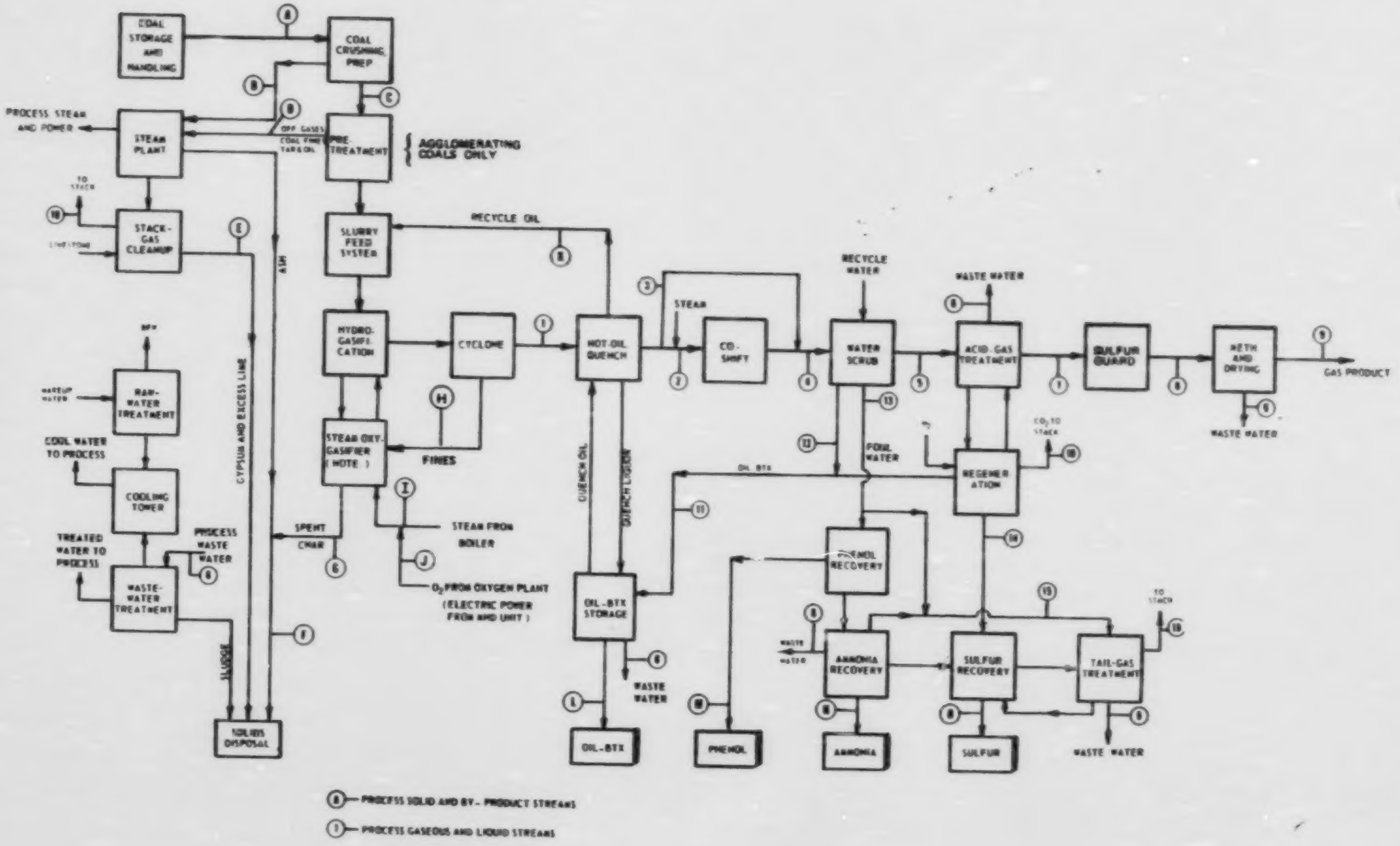
*Metric conversions used —

K (degrees Kelvin) = (°F − 32)/1.8 + 273.15 = °C + 273.15
mol (g)/s = (lb-mol/hr)(0.1259979)
Nm^3/s = (cu ft/day)(3.277432×10^7)
J/s = (Btu/day)(0.01221134)
kN/m^2 = (psia)(6.894757)
kg = (lb)(0.45359237)

Where convenient, the allowed prefixes were substituted for scientific notation. Hence the energy produced by a commercial coal-gasification plant is recorded as 3.0528 GJ/s instead of 3.0528×10^9 J/s (250 billion Btu/day).


COAL STORAGE AND HANDLING
A
COAL CRUSHING, PREP
B
C
PROCESS STEAM AND POWER
STEAM PLANT
D
OFF GASES
COAL FINES
TAR & OIL
PRE-TREATMENT
AGGLOMERATING COALS ONLY
TO STACK
10
STACK-GAS CLEANUP
LIMESTONE
E
ASH
SLURRY FEED SYSTEM
RECYCLE OIL
K
BFW
MAKEUP WATER
RAW-WATER TREATMENT
COOL WATER TO PROCESS
COOLING TOWER
TREATED WATER TO PROCESS
PROCESS WASTE WATER
6
WASTE-WATER TREATMENT
GYPSUM AND EXCESS LIME
SLUDGE
F
SOLIDS DISPOSAL
HYDRO-GASIFICATION
CYCLONE
1
H
STEAM OXY-GASIFIER (NOTE)
FINES
SPENT CHAR
G
I
STEAM FROM BOILER
J
O_2 FROM OXYGEN PLANT (ELECTRIC POWER FROM HMD UNIT)
HOT-OIL QUENCH
QUENCH OIL
QUENCH LIQUOR
OIL-BTX STORAGE
6
WASTE WATER
L
OIL-BTX
3
STEAM
2
CO-SHIFT
4
RECYCLE WATER
WATER SCRUB
13
12
FOUL WATER
OIL BTX
11
PHENOL RECOVERY
M
PHENOL
5
WASTE WATER
6
ACID-GAS TREATMENT
REGENERATION
CO_2 TO STACK
18
14
7
SULFUR GUARD
8
METH AND DRYING
9
GAS PRODUCT
6
WASTE WATER
6
WASTE WATER
AMMONIA RECOVERY
N
AMMONIA
15
SULFUR RECOVERY
O
SULFUR
TO STACK
16
TAIL-GAS TREATMENT
6
WASTE WATER
A — PROCESS SOLID AND BY-PRODUCT STREAMS
1 — PROCESS GASEOUS AND LIQUID STREAMS

NOTE: IN TABLE 3, THE DESIGN BASED ON LIGNITE COAL, THIS UNIT IS AN ELECTROTHERMAL GASIFIER (ETG). SPENT CHAR FROM THE ETG IS CONVEYED TO A HMD UNIT FOR ELECTRIC POWER GENERATION.

Figure 1. PROCESS FLOW DIAGRAM FOR A TYPICAL HYGAS-BASED COMMERCIAL COAL-GASIFICATION PLANT DESIGN

Table 1, Part 1. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING ILLINOIS NO. 6 COAL PRODUCING 84.89 Nm^3/s SNG

Stream Description	Raw Gas		CO-Shift Feed		Shift By-Pass		Combined Feed to Water Scrub Unit		Acid Gas Treatment Feed		Waste Water to Treatment		Feed to Sulfur Guard Unit	
Stream Number	1		2^a		3		4		5		6^b		7	
Temperature, K	590		480		480		325		325				310	
Pressure, kN/m^2	7960		7895		7895		7760		7720				7445	
Component	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %
CO	2925.3	19.84	1950.2	16.74	975.1	22.25	1424.3	8.88	1423.7	12.04			1422.5	18.00
CO_2	2187.2	14.83	1458.2	12.51	729.0	16.64	3691.0	23.[illegible]	3647.1	30.85			11.1	0.14
H_2	3045.0	20.66	2030.0	17.42	1015.0	23.16	4549.3	28.37	4547.3	38.46			4532.3	57.33
H_2O	2457.1	16.66	4525.8	38.84	819.0	18.63	3837.8	23.93	20.8	0.18	6933.4	100.00		
CH_4	1922.7	13.04	1281.8	11.00	641.0	14.63	1922.7	11.99	1921.8	16.26			1916.7	24.25
C_2H_6	63.3	0.43	42.2	0.36	21.0	0.48	63.3	0.39	63.3	0.54			15.0	0.19
C_6H_6	18.8	0.13	12.5	0.11	6.3	0.14	18.8	0.12	17.9	0.15				
NH_3	79.1	0.54	52.8	0.45	26.3	0.60	82.4	0.51			0.03			
HCN	4.9	0.03	3.3	0.03	1.6	0.04	1.6	0.01			0.04			
H_2S	171.6	1.16	114.4	0.98	57.2	1.30	171.1	1.07	169.9	1.44	0.03		Trace	0.10 ppmV
COS	1.5	0.01	1.0	0.01	0.5	0.01	2.0	0.01	2.0	0.02				
N_2	7.4	0.05	4.9	0.04	2.5	0.06	7.4	0.05	7.4	0.06			7.4	0.09
Phenol	1.0		0.6	0.01	0.4	0.01	1.0	0.01			0.03			
Oil	1860.4	12.62	174.6	1.50	87.3	1.99	262.0	1.63	0.8	0.01				
Total	14745.3	100.00	11652.3	100.00	4382.2	100.00	16034.7	100.00	11822.0	100.00	6933.53	100.00	7905.0	100.00

Table 1, Part 2. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING ILLINOIS NO. 6 COAL PRODUCING 84.89 Nm^3/s SNG

Stream Description	Methanation Feed		Gas Product		Waste Gas to Stack		Oil-BTX to Storage		Oil		Foul Water		H_2S to Claus		Scavaged Gas	
Stream Number	8		9		10[c]		11		12		13		14		15	
Temperature, K	310		310													
Pressure, kN/m^2	7410		6895													
Component	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %
CO	1422.5	18.00	3.5	0.10	1.1	0.03					0.6	0.01			0.6	1.2
CO_2	11.1	0.14	4.8	0.13	3237.6	97.84					43.8	0.77	398.4	70.00	43.8	86.45
H_2	4532.3	57.33	235.1	6.54	15.0	0.45					2.0	0.04			2.0	3.97
H_2O			0.3	0.01							5460.5	97.59			0.8	1.49
CH_4	1916.7	24.25	3342.0	93.01	5.2	0.16					0.9	0.02			0.9	1.74
C_2H_6	15.0	0.19			48.3	1.46										
C_6H_6							17.9	6.39			0.9	0.02				
NH_3											82.4	1.46				
HCN											1.6	0.03			1.6	3.16
H_2S					0.04		0.3	0.11	0.2	0.08	1.0	0.02	169.8	29.83	1.0	1.94
COS					0.97	0.03					0.004		1.0	0.17	0.004	0.01
N_2	7.4	0.09	7.4	0.21												
Phenol											1.0	0.02				
Oil					as SO_2 0.92	0.03	261.9	93.50	261.2	99.92						
Total	7905.0	100.00	3593.1	100.00	3309.1	100.00	280.1	100.00	261.4	100.00	5595.7	100.00	569.2	100.00	50.7	100.00

Notes:

[a] 52.03 kg/s of high-pressure steam is added to the CO-shift feed.

[b] Wastewater (6) includes discharges from the acid-gas and tail-gas treatment units, the ammonia recovery unit, oil-BTX storage, and the methanation and drying units. Sampling may be done at the source or at the wastewater-treatment influent pipe. Water is derived from coal in the drying process and elsewhere in the system via condensation. All process water is routed to the wastewater treatment facility for eventual recycling.

[c] Gaseous effluents from the steam plant, tail-gas treatment, and acid-gas regeneration units are included under this column. As in b, above, the sampling may be done at the source or at the influent to the wastewater-treatment plant.

Table 1, Part 3. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING ILLINOIS NO. 6 COAL PRODUCING 84.89 Nm^3/s SNG

Stream Description	Coal Feed from Storage	Coal to Steam Plant	Coal to Pretreater	Pretreatment Gases, Fines, Oil			Gypsum and Excess Lime	Steam Plant Ash and Spent Char
Stream Number	A	B	C	D^a			E	F
	183.92kg/s (6.5% moisture)	38.68kg/s (dry)	133.29kg/s (dry)		gmol/s	mol %	13.86 kg/s	23.6 kg/s
Component *	wt. % dry							
C	69.40			CO	199.9	3.49		
H	4.80			CO_2	358.6	6.26		10.3% Carbon
O	8.71	Ultimate analysis of composite bituminous coal sample is the same as stream A. (Illinois No. 6 Seam)		H_2				
N	1.35			H_2O	1152.0	20.11		
S	4.20			CH_4	26.3	0.46		0.3% Sulfur
Ash	11.54			C_2H_6	13.2	0.23		
Total	100.00			C_3H_8	26.3	0.46		
				H_2S				
				N_2	3728.8	65.09		
				O_2	135.8	2.37		
				Ar	48.1	0.84		
				SO_2	39.5	0.69		
				Total	5728.5	100.00		

* Note other elements shown in Table 4.

Table 1, Part 4. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING ILLINOIS NO. 6 COAL PRODUCING 84.89 Nm^3/s SNG

Stream Description	Cyclone Fines	Steam To OG	Oxygen To OG	Recycle Oil	By Product Oil-BTX		By Product Phenols		By Product Ammonia		By Product Sulfur	
Stream Number	H[b]	I	J	K	L		M		N		O	
	22.22 kg/s	124.70 kg/s	34.06 kg/s	215.79 kg/s	5.01 kg/s		0.16 kg/s		1.40 kg/s		7.08 kg/s	
Component				gm mol/s	gm mol/s		gm mol/s		gm mol/s		gm mol/s	
C	75.60			1598.4	C_6H_6	17.9	C_6H_6	0.88	NH_3	82.4	Sulfur	220.98
H	2.24			(oil mol. wt. 135)	H_2S	0.3	Phenol	0.98				
O	3.46				Oil	26.7						
N	1.38											
S	1.46											
Ash	15.86											
Total	100.00					44.9		1.86		82.4		220.98

Notes:

[a] The pretreater effluent includes 5728.5 g-mol/s off-gases, 0.35 kg/s tar and oils, and 1.56 kg/s coal fines – to be used as fuel for steam generation. See Appendix A for an analysis of tars and oils from the HYGAS pretreater and from the Synthane gasification process.

B75030539d

[b] Of these cyclone fines, 44.9% are less than 325 mesh (< 44 μm).

Table 2, Part 1. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING MONTANA SUBBITUMINOUS COAL PRODUCING 85.21 Nm^3/s SNG

Stream Description	Raw Gas		CO-Shift Feed		Shift By-Pass		Combined Feed to Water Scrub Unit		Acid Gas Treatment Feed		Waste Water to Treatment		Feed to Sulfur Guard Unit	
Stream Number	1		2[a]		3		4		5		6[b]		7	
Temperature, K	590		480		480		325		325				310	
Pressure, kN/m^2	7960		7895		7895		7760		7720				7445	
Component	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %
CO	3548.2	21.97	2365.5	19.31	1182.7	24.99	1660.3	9.78	1659.6	12.89			1658.3	19.29
CO_2	2277.7	14.11	1518.5	12.40	759.1	16.04	4166.6	24.54	4122.8	32.02			12.6	0.15
H_2	3420.6	21.18	2280.1	18.62	1140.2	24.09	5309.6	31.26	5307.5	41.22			5288.8	61.51
H_2O	2870.4	17.81	4700.7	38.38	960.1	20.27	3770.9	22.20	22.7	0.18	7191.9	100.00		
CH_4	1576.0	9.76	1050.7	8.58	525.3	11.10	1576.0	9.28	1575.1	12.24			1568.5	18.24
C_2H_6	127.6	0.79	85.0	0.69	42.6	0.90	127.6	0.75	127.6	0.99			67.2	0.78
C_6H_6	28.3	0.18	18.9	0.15	9.4	0.70	28.3	0.17	27.5	0.21				
NH_3	24.7	0.15	16.5	0.13	8.2	0.17	25.7	0.15			5 ppmW			
HCN	1.5	0.01	1.0	0.01	0.5	0.01	0.5				12 ppmW			
H_2S	30.2	0.19	20.1	0.16	10.1	0.21	30.1	0.18	28.8	0.22	0.2 ppmW		Trace	0.1 ppmW
COS	0.3		0.2		0.1		0.3		0.3					
N_2	2.3	0.01	1.5	0.01	0.8	0.02	2.3	0.01	2.3	0.02			2.3	0.03
Phenol	1.0	0.01	0.6	0.01	0.4	0.01	1.0	0.01			20 ppmW			
Oil	2233.0	13.83	188.7	1.54	94.3	1.99	283.0	1.67	0.8	0.01				
Total	16147.8	100.00	12248.5	100.00	4733.7	100.00	16982.2	100.00	10459.	100.00	7191.9	100.00	8597.7	100.00

Table 2, Part 2. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING MONTANA SUBBITUMINOUS COAL PRODUCING 85.21 Nm^3/s SNG

Stream Description	Methanation Feed		Gas Product		Waste Gas To Stack		By-Product Oil-BTX		Oil		Foul Water		H_2S To Claus		Scavaged Gas	
Stream Number	8		9		10[c]		11		12		13		14		15	
Temperature, K	310		310													
Pressure, kN/m^2	7410		6895													
Component	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %	gm mol/s	mol %
CO	1658.3	19.29	3.5	0.10	1.4	0.03					0.6	0.01			0.6	1.27
CO_2	12.6	0.15	6.9	0.19	4043.1	97.86					43.8	0.79	67.0	70.00	43.8	88.37
H_2	5288.8	61.51	235.1	6.51	18.8	0.46					2.0	0.04			2.0	4.06
H_2O			0.3	0.01							5496.7	98.63			0.8	1.52
CH_4	1568.5	18.24	3363.3	93.13	6.6	0.16					0.9	0.02			0.9	1.79
C_2H_6	67.2	0.78			60.5	1.46										
C_6H_6							27.5	8.84			0.9	0.02				
NH_3											25.7	0.46				
HCN											0.5	0.01			0.5	1.02
H_2S					0.04		0.5	0.16	0.38	0.13	1.0	0.01	28.6	29.86	9.8	1.98
COS					0.16	0.01					2 ppmW		0.16	0.14	76 ppmV	
N_2	2.3	0.03	2.3	0.06												
Phenol											1.0	0.01				
Oil					SO_2 0.84	0.02	283.0	91.00	282.22	99.87						
Total	8597.6	100.00	3611.4	100.00	4131.44	100.00	311.0	100.00	282.6	100.00	5573.1	100.00	95.76	100.00	58.4	100.00

Notes:

[a] 50.16 kg/s of high-pressure steam are added to the CO-shift feed.

[b] Five wastewater streams are combined under this heading: acid gas, tail-gas treatment, the ammonia recovery unit, oil-BTX storage, and methanation and drying wastewater. Wastewater sampling may be done at each source separately or at the wastewater-treatment influent pipe.

[c] Three waste gas streams are combined here: steam plant, tail-gas treatment, and acid-gas regeneration gas streams. Samplings may be done at each source or in the stack.

Table 2, Part 3. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING MONTANA SUBBITUMINOUS COAL PRODUCING 85.21 Nm^3/s SNG

Stream Description	Coal Feed from Storage	Coal to Steam Plant	Coal to Slurry Feed System	Pretreatment Off Gases, Fines, Tars	Gypsum and Excess Lime	Steam Plant Ash and Spent Char
Stream Number	A	B	C	D[a]	E[b]	F
	248.61 kg/s (22% Moisture)	48.72 kg/s (6.5% Moisture)	158.68 kg/s (6.5% Moisture)		2.18 kg/s	20.20 kg/s
Component[*]	wt % dry	wt % dry	wt % dry			
C	68.12					10.2% Carbon
H	4.64					
O	18.57					
N	0.85					
S	0.66	Ultimate analysis of composite subbituminous coal samples is the same as stream A. (Montana subbituminous)				
Ash	7.16					0.7% Sulfur
Total	100.00					

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[*] Note other elements shown in Table 6.

Table 2, Part 4. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING MONTANA SUBBITUMINOUS COAL PRODUCING 85.21 Nm^3/s SNG

Stream Description	Cyclone Fines	Steam to OG	Oxygen to OG	Recycle Oil	By-Product Oil-BTX	By-Product Phenols	By-Product Ammonia	By-Product Sulfur
Stream Number	H[c]	I	J	K	L	M	N	O
	24.73 kg/s	114.32 kg/s	38.1 kg/s	263.3 kg/s	8.93 kg/s	0.16 kg/s	0.44 kg/s	1.22 kg/s
				gm mol/s	gm mol/s	gm mol/s	gm mol/s	gm mol/s
Component								
C				1950.1	C_6H_6 27.5	C_6H_6 0.88	NH_3 25.7	Sulfur 38.16
				(Oil mol.wt. 135)	H_2S 0.5			
H					Oil 50.1	Phenol 1.01		
O								
N								
S								
Ash								
					78.1	1.89	25.7	

Notes:

[a] Pretreatment, to remove coal agglomerating tendencies, is not required for Montana subbituminous coal. Fines are produced in the grinding and crushing operation that will be used to fuel the steam boiler.

[b] Sulfur content of Montana subbituminous is generally <1%. This value of gypsum and excess lime has been correlated from data on Illinois No. 5 coal with 4.45 per cent sulfur. It is possible that the SO_2 in the steam-plant stack gas may be low enough to eliminate the need for lime or any other form of treatment

[c] The ultimate analysis of the cyclone fines is not available for subbituminous coal.

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Table 3, Part 1. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING LIGNITE COAL[a] PRODUCING 85.78 Nm³/s SNG

Stream Description	Raw Gas		CO-Shift Feed		Shift By-Pass		Combined Feed to Water Scrub Unit		Acid Gas Treatment Feed		Waste Water to Treatment		Feed to Sulfur Guard Unit	
Stream Number	1		2[b]		3		4		5[c]		6[d]		7[c]	
Temperature, K	600		600				685		310		310		310	
Pressure, kN/m²	7685		7550				7480		7445				7340	
Component	gm mol/s	mol %	gm mol/s	mol%	gm mol/s	mol%	gm mol/s	mol%	gm mol/s	mol%	gm mol/s	mol%	gm mol/s	mol %
CO	1553.2	11.42	1553.2	13.95			781.9	7.55	781.9	7.69			781.9	12.97
CO_2	2006.1	14.75	1905.8	17.12			1905.8	18.39	1866.2	18.35	14.0	0.13	60.3	1.00
H_2	1960.1	14.42	1960.1	17.60	N/A		2731.4	26.36	2731.4	26.87			2731.4	45.31
H_2O	4015.7	29.53	3054.4	27.43			2283.1	22.03	2283.1	22.46	11110.7	99.86	7.8	0.13
CH_4	2252.0	16.56	2252	20.23			2252.0	21.73	2252.0	22.15			252.0	37.35
C_2H_6	109.7	0.81	109.7	0.99			109.7	1.06	109.7	1.08			109.7	1.82
C_3H_8	36.7	0.27	36.7	0.33			36.7	0.35	36.7	0.36			36.7	0.61
C_6H_6	18.2	0.14	23.3	0.21			23.3	0.23	2.4	0.02				
H_2S	44.3	0.33	44.3	0.40			44.3	0.43	42.6	0.42	1.7	0.01		
NH_3	27.8	0.20	27.8	0.25			27.8	0.27						
N_2	48.6	0.36	48.6	0.44			48.6	0.47	48.6	0.48			48.6	0.81
Oil	1524.7	11.21	116.8	1.05			116.8	1.13	11.7	0.12				
Total	13597.1	100.00	11132.7	100.00			10361.4	100.00	10166.3	100.00	11126.4	100.00	6028.4	100.00

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Table 3, Part 2. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING LIGNITE COAL PRODUCING 85.78 Nm^3/s SNG

Stream Description	Methanation and Drying		Product Gas		Process Waste Gas		Oil-BTX to Storage		Oil		Foul Water		H_2S To Claus		Scavaged Gases	
Stream Number	8		9		10[e]		11		12		13		14		15	
Temperature, K	310		310		390		310		310		310		310		310	
Pressure, kN/m^2	7340		6995		7445		7340		7340		7340		7340		7340	
Component	gm mol/s	mol %	gm mol/s	mol%	gm mol/s	mol%	gm mol/s	mol %	gm mol/s	mol%	gm mol/s	mol%	gm mol/s	mol%	gm mol/s	mol %
CO	781.9	12.97	3.7	0.10												
CO_2	60.3	1.00	46.3	1.28	1734.9	100.00					39.6	0.62	71.04	63.38		
H_2	2731.4	45.31	157.6	4.34												
H_2O	7.8	0.13	0.5	0.01							6284.4	98.88			N/A	
CH_4	2252.0	37.35	3373.7	92.93												
C_2H_6	109.7	1.82														
C_3H_8	36.7	0.61														
C_6H_6							23.3	16.91	19.8	16.01	1.1	0.02				
H_2S											1.7	0.03	40.9	36.49		
NH_3											27.8	0.43	0.14	0.13 (COS)		
N_2	48.6	0.81	48.6	1.34												
Oil							114.5	83.09	103.9	83.99	1.2	0.02				
	6028.4	100.00	3630.4	100.00	1734.9	100.00	137.8	100.00	123.7	100.00	6355.8	100.00	112.1	100.00		

Notes:

[a] The flow rates and stream compositions listed in this table are approximate, having been derived from an early design based on lignite coal. Where stream compositions are unspecified, the original design data were judged inappropriate for inclusion.

[b] The H_2O flow rate in stream 2 reflects the addition of 52.47 kg/s of reaction steam to the CO-shift reactor.

[c] Streams 5 and 7 are approximate. The early design included a purification unit prior to the gas-shift reactor to remove CO_2 and H_2S, and another unit following the gas-shift reactor to remove H_2O, benzene, CO_2, and any remaining H_2S from the product-gas stream.

[d] Wastewater to the water treatment facility, is collected from the coal-drying units, the quench tower, purification unit, the methanation unit, and the product-gas dryer.

[e] CO_2 from the acid-gas treatment only.

Table 3, Part 3. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING LIGNITE COAL PRODUCING 85.78 Nm^3/s SNG

Stream Description	Coal Feed from Storage	Coal to Dryer, Offsite	Coal to Slurry Feed System	Pretreater Gases, Fines, Oil	Gypsum and Excess Lime	Ash	Electro-gasified Char to MHD and Boile
Stream Number	A	B[a]	C	D[b]	E[c]	F	G
	292.1 kg/s (35% Moisture)	19.7 kg/s (35% Moisture)	272.4 kg/s (35% Moisture)		3.43 kg/s	23.62 kg/s	49.00 kg/s
Component*							
C	65.45					8.2% Carbon	67.75
H	4.45	Ultimate analysis of composite lignite coal samples is the same as stream A. (Montana lignite)					0.00
O	19.85						0.12
N	0.92						0.54
S	0.78					0.07% Sulfur	0.72
Ash	8.55						30.87
Total	100.00						100.00

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*Note other elements shown in Table 7.

Table 3, Part 4. STREAM COMPOSITIONS AND FLOW RATES FOR HYGAS-BASED COMMERCIAL GASIFICATION PLANT USING LIGNITE COAL PRODUCING 85.78 Nm^3/s SNG

Stream Description	Cyclone Fines	Steam From Boiler	Electric Power To ETG	Recycle Slurry Oil	By-Product Oil-BTX	By-Product Phenols	By-Product Ammonia	By-Product Sulfur
Stream Number	H^d	I	J	K	L^e	M^e	N^e	O^e
	29.5 kg/s	54.6 kg/s	2.4TJ	109.6 kg/s	10.7 kg/s	0.19 kg/s	0.47 kg/s	1.36 kg/s
				1402.8 gm mol/s	93.2 gm mol/s	2.3 gm mol/s	27.8 gm mol/s	42.6 gm mol/s
Component								
C	58.9							
H	3.15							
O	10.67							
N	0.99							
S	0.84							
Ash	25.45							
Total	100.00							

Notes:

[a] This quantity of coal is conveyed to a packaged steam boiler and to a MHD unit to generate electricity for an electrothermal gasifier (ETG).

[b] Lignite does not require pretreatment.

[c] The value is proportionate to a design based on bituminous coal.

[d] Of these cyclone fines, 43.5% are less than 325 mesh. (<44 μm)

[e] The flow rates of these streams are computed in proportion to values from a Montana subbituminous design and are approximations.

Typical operating temperatures (in K) and pressures (in kN/m^2) are listed for the process streams where this information is available. Solid and by-product streams are assumed to be at ambient conditions. The flow rates of the process streams are calculated and tabulated in kilograms per second (kg/s) or moles per second (mol/s). Both are SI-approved notations.[12, 53] This test plan could be applied to other gasification processes without major alterations, even though it is written specifically for the HYGAS Process.

Coals

The proximate and trace-element analyses of coals may vary considerably from mine to mine, or even from seam to seam. Therefore, it is imperative that a test plan be flexible enough to allow for fluctuations in feed composition or process conditions that might occur during gasification. For this reason, process mass balances for three different coals are presented instead of one mass balance for an "average" coal, which may not exist. Each of the mass balances in Tables 1, 2, and 3 is based upon the ultimate analysis of a composite of several coal samples from the same seam. We believe this approach is valid and representative, even though the properties of certain coals necessitate the use of special handling and pretreatment steps prior to gasification.

Coal Pretreatment

Bituminous coals have significant agglomerating tendencies which must be removed prior to gasification. If fed directly to the gasifier, a bituminous coal would agglomerate, form clinkers, and plug the reactor. One method of removing the sticking property is to mildly oxidize the feed material (at 700 K) to drive off some volatile matter and to cover each particle with a nonsticking layer of oxidized material.

The pretreatment process involves the production of sizable quantities of off-gases, coal fines, tars, and oils which must be utilized in some way or discarded. Significant quantities of certain trace and minor elements are also volatilized during pretreatment, contributing to the overall losses as shown in Table 4, Column D.

Table 4. CALCULATED FLOW RATES OF TRACE AND MINOR ELEMENTS IN A HYGAS-BASED, COMMERCIAL COAL GASIFICATION PLANT USING ILLINOIS No. 6 SEAM BITUMINOUS COAL

Stream Description	Coal Feed to Pretreater		Pretreater Losses[a]	Oxygasifier Char	Hot Oil Quench	Water Scrub[b]	Acid-Gas Effluent[c]	Sulfur Guard	Methanation Condensate[d]	Product Gas
Stream Number	C		D	G	K	12, 13	11, 14	P	6	9
Element	ppm*	kg/s (X 10³)	kg/s (X 10³)							
Sb	1.1	0.15	0.043	0.096	0.008	0.003	0.0	0.0	0.0	0.0
As	24	3.2	0.35	2.1	0.3	0.2	0.25	0.0	0.0	0.0
Ba	31	4.1	0.0	4.1	0.0	0.0	0.0	0.0	0.0	0.0
Be	1	0.13	0.02	0.10	0.01	0.0	0.0	0.0	0.0	0.0
Bi	1.1	0.15	0.022	0.072	0.050	0.0	0.0	0.0	0.0	0.0
B	200	27.0	0.73	24.0	2.0	0.27	0.0	0.0	0.0	0.0
Cd	0.89	0.12	0.044	0.028	0.040	0.008	0.0	0.0	0.0	0.0
Ca	3500	470.0	100.0	310.0	60.0	0.0	0.0	0.0	0.0	0.0
Cl	2300	310.0	110.0	80.0	5.0	110.0	4.0	1.0	0.0	0.0
Cr	15	2.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0
Co	3.6	0.48	0.0	0.48	0.0	0.0	0.0	0.0	0.0	0.0
Cu	19	2.5	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0
F	61	8.1	0.29	6.0	0.5	0.81	0.5	0.0	0.0	0.0
Ge	4.3	0.57	0.033	0.52	0.015	0.002	0.0	0.0	0.0	0.0
Fe	14,000	1870.0	73.0	1730.0	65.0	2.0	0.0	0.0	0.0	0.0
Pb	11	1.5	0.73	0.77	0.0	0.0	0.0	0.0	0.0	0.0
Li	33	4.4	0.0	4.4	0.0	0.0	0.0	0.0	0.0	0.0
Mg	570	76.0	0.0	76.0	0.0	0.0	0.0	0.0	0.0	0.0
Mn	48	6.4	0.50	5.2	1.1	0.1	0.0	0.0	0.0	0.0
Hg	0.12	0.016	0.013	0.0006	0.0013	0.0006	0.0004	0.0001	0.0	0.0
Mo	7.0	0.933	0.02	0.906	0.007	0.0	0.0	0.0	0.0	0.0
Ni	15	2.0	0.09	1.9	0.01	0.0	0.0	0.0	0.0	0.0
N	10,400	1390.0	0.0	320.0	70.0	950.0	40.0	9.0	1.0	0.0
K	1700	227.0	0.0	227.0	0.0	0.0	0.0	0.0	0.0	0.0
Sm	0.74	0.098	0.0	0.098	0.0	0.0	0.0	0.0	0.0	0.0
Se	13	1.7	0.24	1.0	0.1	0.20	0.16	0.0	0.0	0.0

* Parts per million

Table 4, Cont. CALCULATED FLOW RATES OF TRACE AND MINOR ELEMENTS IN A HYGAS-BASED, COMMERCIAL COAL GASIFICATION PLANT USING ILLINOIS No. 6 SEAM BITUMINIOUS COAL

Stream Description	Coal Feed to Pretreater		Pretreater Losses[a]	Oxygasifier Char	Hot Oil Quench	Water Scrub[b]	Acid-Gas Effluent[c]	Sulfur Guard	Methanation Condensate[d]	Product Gas
Stream Number	C		D	G	K	12, 13	11, 14	P	6	9
Element	ppm*	kg/s ($\times 10^3$)	kg/s ($\times 10^3$)							
Si	20,000	2670.0	0.0	2670.0	0.0	0.0	0.0	0.0	0.0	0.0
Ag	0.1	0.013	0.0042	0.0048	0.003	0.001	0.0	0.0	0.0	0.0
Na	1400	187.0	0.0	187.0	0.0	0.0	0.0	0.0	0.0	0.0
Sr	37	4.9	0.0	4.9	0.0	0.0	0.0	0.0	0.0	0.0
S	38,000	5100	1150.0	1040.0	120.0	200.0	2570.0	20.0	0.0	0.0
Te	8.1	1.08	0.25	0.64	0.09	0.05	0.05	0.0	0.0	0.0
Sn	2.0	0.27	0.07	0.13	0.06	0.01	0.0	0.0	0.0	0.0
Ti	770	103.0	0.0	100.0	3.0	0.0	0.0	0.0	0.0	0.0
V	17	2.3	0.21	1.9	0.16	0.03	0.0	0.0	0.0	0.0
Yb	0.56	0.075	0.0027	0.069	0.003	0.0003	0.0	0.0	0.0	0.0
Zn	49	6.5	0.99	4.8	0.60	0.11	0.0	0.0	0.0	0.0
Zr	35	4.7	0.0	4.7	0.0	0.0	0.0	0.0	0.0	0.0

Notes:

[a] Pretreater losses arise from the volatilization of elements at lower temperatures (700K), and are in the form of tars, oils, fines, and off-gases. All of this material is burned in the steam plant. Volatile compounds may be lost to the stack unless cleaned by scrubbing or some other method. Figure 1 incorporates a calcite scrubber to remove SO_2 from the stack gas.

[b] Two streams are split here: The oil stream is recycled to the slurry preparation and may accumulate trace elements. The water stream contains phenols, NH_4-(F, Cl) to be separated, and the treated water to be recycled. It is important to note that the by-products may show enrichment of some trace elements.

[c] The sour gas from the acid-gas treatment unit is sent to the Claus plant. It contains much of the acidic compounds of CO_2, H_2S, As_2O_3, B_2O_3, etc., and fine particulates. Oil is separated during regeneration and is recycled. CO_2 is released to the atmosphere with trace sulfur compounds. Some gaseous, acidic elements, i.e., H_2Se and H_2Te, will most likely end up in the Claus plant sulfur product.

[d] Water is condensed during methanation and may carry away other trace elements. Almost total sulfur removal is accomplished during methanation by adsorption onto the catalyst particles. The product gas will be analyzed for the more volatile, toxic elements, but not for the innocuous ones.

In the HYGAS process description (Figure 1, Table 1), the pretreater by-products are consumed in the boiler for steam production. The primary boiler fuel is coal, while pretreatment fuels provide a supplement. The combined combustion gases from these fuels represent a considerable source of potential pollutants, which may require the addition of larger (but not more complex) atmospheric emission controls to the stack. Those materials removed from the coal during pretreatment must be cleaned from the stack gas, rather than handled in the normal gasification cleanup train. For example, pretreatment of high-sulfur coals may volatilize 30% of the sulfur as sulfur oxides, which would otherwise be removed during the acid-gas treatment step as hydrogen sulfide.

By eliminating the coal pretreatment step (by mild oxidation) through process modifications and improvements, the overall gasification process would be simplified, while the demands on the steam plant stack-gas cleanup system would be reduced.

Coal Energy and Moisture Content

Lignite and subbituminous coals have low (<1%) sulfur contents and low agglomerating tendencies that make them the most "well-behaved" and environmentally sound fuels for gasification. However, each of these coals has a higher moisture content and lower heating value than the bituminous coal. Taken together, these factors require that much larger quantities of lignite and subbituminous coal be conveyed to a gasification plant, in order to produce the same quantity of SNG as would be obtained from bituminous coal. For example, to produce 3.0528 GJ/s (250 X 10^9 Btu/day) of SNG requires a lignite coal feed rate of 292.09 kg/s (27,818 tons/day) to the gasification plant. The corresponding flow rate for subbituminous coal is 248.61 kg/s (23,678 tons/day), and for bituminous, 183.92 kg/s (17,516 tons/day). The lignite flow rate is 59% higher than the bituminous flow rate. Two factors can be considered here. First, in each design the total coal energy conveyed to the gasification plant is within 1.5% of the others. The totals range from 4.9902 GJ/s for lignite to 5.0750 GJ/s for subbituminous. Second, of the 292.09 kg/s of lignite feed, 102.23 kg/s (35%) is moisture, much of which must be removed from the coal before gasification. A summary of the heating values (HHV), moisture contents, and process mass and energy flow rates for three coals is shown below. Note that the quantities of coal energy to the "Process" and to the "Offsites" are quite similar for the bituminous and subbituminous coals, differing from each other by less than 1% and 5%, respectively.

Coal	Moisture Content	Heating Value, Dry Basis	Raw Coal to Plant	Coal to Process	Coal to Offsites	Product SNG Energy	Process Efficiency
	%	MJ/kg (Btu/lb)	GJ/s (kg/s)				%
Lignite[a]	35	26.2839 (11,300)	4.9902 (292.09)	4.6532 (272.36)	0.3370 (19.72)	3.0528	71.7
Subbituminous	22	26.2865 (11,301)	5.0750 (248.61)	3.8828[b] (158.68)	1.1922[b] (48.72)	3.0528	67.2
Bituminous	6.5	29.3142 (12,603)	5.0513[c] (183.29)	3.9151[c] (133.29)	1.1362[c] (38.68)	3.0528	66.2

[a] A magnetohydrodynamic (MHD) unit provided energy for an electrothermal gasifier in this design.

[b] Partially dried coal contains 6.5% moisture.

[c] Dried coal contains <1% moisture.

The overall energy efficiency for the subbituminous design is 67.2%, that for the bituminous design is 66.2%. Because of the use of a magnetohydrodynamic unit for electric power generation in the lignite design, the energy requirements are not comparable to the other two designs. However, the efficiency of this early lignite-based design was calculated at 71.7%.

Modes of Occurrence of Trace and Minor Elements in Coals

Trace and minor elements are present in raw coals, both in the mineral matter and in association with the organic materials. Many are present as sulfides, or in weathered coals as sulfates[43,50]. Nitrogen is present almost exclusively in five-to-six-member organic ring compounds.[34] Sodium chloride deposited from saline ground water, is assumed to be the predominant source of chlorine in coal.[45,50] Nitride compounds have not as yet been detected in coal. Carbide compounds also have not been observed in coals, or to any extent in nature (except in iron meteorites and some terrestrial iron[41]).

The modes of occurrence vary, yet there is evidence in the literature that one or two forms of each element predominate.[6,7,20,34,45,50] A summary of the typical modes of occurrence of trace and minor elements in coals as reported in the literature is presented in Table 5.

Whenever literature searches failed to indicate the naturally occurring form of an element in coal, its periodic properties and trends were followed. For example, data on the occurrence of bismuth in coal is scant, but one may anticipate that bismuth and lead would occur in similar compounds. Hence bismuth is listed in the table as a sulfide, as is lead.

A study by Ruch et al.[50] included a matrix of population correlation coefficients for potentially volatile trace elements in coal samples, which was useful in the development of Table 5. The matrix indicated how frequently one element was detected in a sample relative to the presence of another element. For example, the highest correlation coefficient, 0.93, occurred for the zinc-cadmium pair. These two elements are frequently observed together in coal in the mineral sphalerite (zinc sulfide).

To expedite thermodynamic calculations in a later section of this report, the element forms listed in Table 5 are assumed to be the only ones present in the raw coal. Because each element has undergone a thorough thermodynamic evaluation, errors in this assumption (and therefore in the table) will not significantly affect the outcome of the analysis. If bismuth naturally occurs in coal as an oxide and not as a sulfide as assumed, the results of the test plan analysis would be the same. This is assured, because the same reaction calculations have been carried out for both the sulfide and the oxide forms of bismuth. (See Appendix E, Table E-2, Part 1.) If the necessary thermodynamic data for an element form are not available (as in the case of bismuth sulfate), periodic property extrapolation must be depended upon for the analysis. The analyses of every element in this study are dependent upon the availability of accurate and reliable thermodynamic data. Where data are lacking, that part of the analysis is incomplete.

Table 5. TYPICAL MODES OF OCCURRENCE OF TRACE AND MINOR ELEMENTS IN COAL

Element	Mode	Element	Mode
Sb	Sulfide	Mo	Sulfide
As	Oxide, sulfide	Ni	Sulfide
Ba	Carbonate, sulfate with Ca	N	OC
Be	OC[*]	K	KCl, carbonate
Bi	Sulfide	Sm	SQ
B	OC, borate	Sc	Oxide
Cd	Sulfide	Se	POC, sulfide, iron selenides
Ca	Oxide, carbonate, sulfate	Si	Oxide, SQ
Cl	POC[†], sodium chloride	Ag	Element, sulfide, SQ
Cr	POC, oxide	Na	POC, carbonate
Co	POC, sulfide	Sr	POC, with Ca
Cu	$CuFeS_2$, sulfide	S	POC, sulfides, sulfates
F	CaF_2	Te	Iron tellurides
Ge	POC, carbonate	Th	SQ
Fe	Carbonate, sulfide, oxide	Sn	Carbonate, sulfide
Pb	Sulfide	Ti	POC, SQ
Li	SQ[‡]	V	OC
Mg	POC, carbonate, SQ	Yb	SQ
Mn	Carbonate in $CaCO_3$, SQ	Zn	Sulfide
Hg	POC, element, sulfide	Zr	Oxide, SQ

[*] OC - organic contribution.

[†] POC - partial organic contribution.

[‡] SQ - silicates, clay, quartz.

Coal Ash Materials

The mineral matter of coal is comprised of materials which may undergo reactions with process gases in the hydrogasifier. These materials include silicates, calcite, alumina, tungstates, etc. Thermodynamic data for many of the compounds are available, and further work should include an investigation of their reactions in the hydrogasifier's fluidized bed.

There is a synergistic effect between chlorine and trace elements during combustion.[16] The presence of chlorine increases the volatilization of elemental forms, such as arsenious oxide (As_2O_3). On combustion, As_2O_3 volatilizes unless retained as arsenate or arsenites by carbonate minerals, such as dolomite ($CaCO_3 \cdot MgCO_3$) or barite ($BaCO_3$), among others. Perhaps by reducing the chlorine content (as hydrochloric acid) from the gasifier or by increasing the carbonate content, the trace elements may tend to remain with the ash rather than be volatilized.

Possible Disposition of Trace and Minor Elements

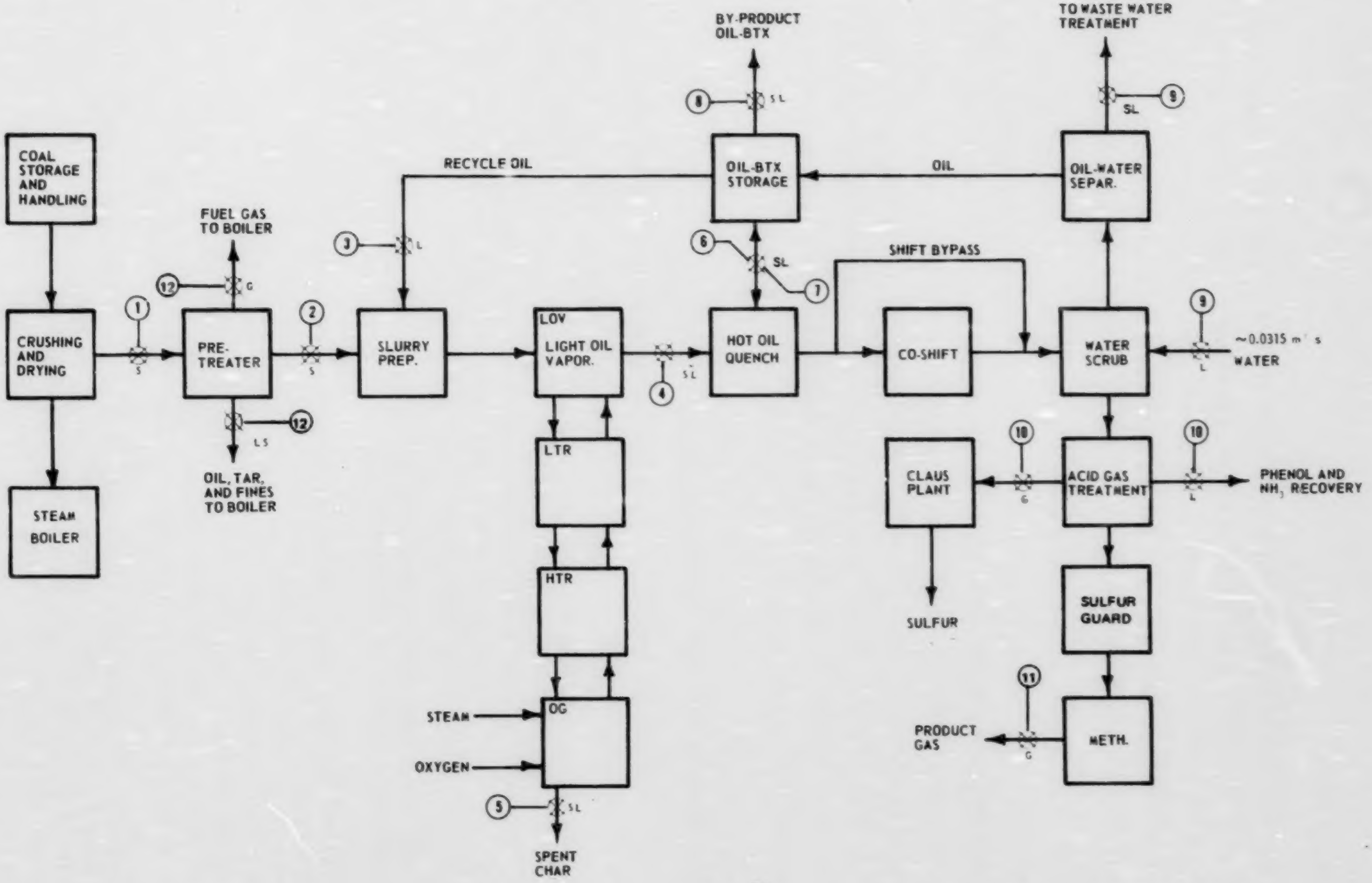
Trace elements in the feed to a commercial coal-gasification plant are subject to a number of reactions. The possible fates of these materials are listed below with reference to Figure 2.

1. Coal storage and handling losses arise from the leaching of trace elements from coal piles by rain water. Windborne dust losses must be minimized.

2. The coal crushing and drying process will produce wastewater that may contain trace elements.

3. During pretreatment at 700K, certain trace elements, such as mercury or lead, may be volatilized to the fuel gas either in the vapor phase or adsorbed on particulates. Oil, tar, and fines resulting from pretreatment may also contain trace and minor elements. This material is combusted along with the fuel gas and is subjected to the stack gas emission controls. Thus, some volatile trace elements may be lost to the stack gas.

4. In the light-oil vaporizer (LOV), the light oil is flashed and the coal dried prior to gasification. Organic material, which is soluble in light oil (organometallic compounds and/or metal chelates) may in part be flashed directly overhead, condensed


COAL STORAGE AND HANDLING
CRUSHING AND DRYING
STEAM BOILER
FUEL GAS TO BOILER
PRE-TREATER
OIL, TAR, AND FINES TO BOILER
SLURRY PREP.
RECYCLE OIL
LOV
LIGHT OIL VAPOR.
LTR
HTR
OG
STEAM
OXYGEN
SPENT CHAR
HOT OIL QUENCH
BY-PRODUCT OIL-BTX
OIL-BTX STORAGE
OIL
OIL-WATER SEPAR.
TO WASTE WATER TREATMENT
SHIFT BYPASS
CO-SHIFT
WATER SCRUB
~0.0315 m³/s
WATER
CLAUS PLANT
SULFUR
ACID GAS TREATMENT
PHENOL AND NH₃ RECOVERY
SULFUR GUARD
METH.
PRODUCT GAS
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
S
L
G
SL
LS

SLG — Locations of SOLID (S), LIQUID (L), or GASEOUS (G) Sampling

Stream numbers refer to those in Section IV, Table [illegible]

Figure 2. POSSIBLE DISTRIBUTION OF TRACE AND MINOR ELEMENTS

in the hot-oil quench unit, and thus recycled to slurry preparation. Part of this material is expected to accompany the coal to the hydrogasifier stage and react with HYGAS Process gases. The unquenched fraction of organic material may pass through the CO-shift reactor and be removed in the water scrub unit. The organic phase is separated and recycled to the slurry preparation unit; the aqueous phase is piped to the wastewater treatment area. Coal fines not cycloned out and recycled to the hydrogasifier may be entrained overhead. Extremely fine particulates may pass completely through the plant, possibly as fumes. It is important to note that these particulates may be enriched in volatile trace elements due to condensation in the LOV.[39]

5. Other volatile trace elements may neither be condensed in the LOV nor removed during the subsequent quenching and scrubbing operations, but remain in the process gas stream. These compounds, or elements, will be removed in either the acid-gas treatment unit or the caustic scrub prior to methanation.

6. The coal feed material flows by gravity to the low- and high-temperature reactors, where it is partially gasified. The char goes to the steam-oxygen gasifier (OG), where the remaining carbon is gasified. The mineral matter in the feed ultimately exits from the OG as low-carbon-content ash.

7. Some trace-element losses may be attributed to plating of the material onto the surfaces of the reactor and other process units. Similarly, some sulfur compounds will be adsorbed onto the catalyst particles in either the gas shift or methanation reactors, resulting in the poisoning of the catalysts.

8. Product streams from the purification units may contain trace elements in the by-product oil-BTX, phenol, ammonia, sulfur, and spent caustic.

These paths are many and varied, with complex mechanisms for each. The calculations indicate the streams in which an element is likely to appear; however, the element may appear much earlier or somewhat later than predicted. This depends in part on the nature of the coal and on its trace-element composition.

Fluctuations in the process pressure or temperature will not substantially affect the appearance of the trace elements down stream unless the variations of temperature or pressure are extreme. (See "Variability of Operating Conditions," page 36.) A rapid increase in either parameter would trigger automatic controls that would shut down the reactor.

However, process fluctuations compound the problems associated with closing the mass balance around the plant, especially for the toxic elements mercury, selenium, arsenic, cadmium, lead, and antimony. An analysis of the gas from the Synthane Process done by Forney et al.[18] showed that mercury was present in the gas from the gasifier but not in the final product. The product gas from the HYGAS plant should be analyzed for volatile trace elements, but is expected that, as in the Synthane product gas, their levels will be very low[18], perhaps because of amalgamation on colder parts of the methanation catalyst bed.

Thermodynamically Stable Forms of the Elements in HYGAS Process Units

With the information in Table 5, free-energy calculations were performed to determine the most stable forms of each feed species in the pretreater, the hydrogasifier, and the CO-shift reactor. Thus, each element was followed thermodynamically through the process to estimate its ultimate form and distribution. The effect of individual reaction kinetics was not included in this development and each reaction was assumed to go to an equilibrium condition. Some of the reactions which are likely to occur in each of the process units are included below, along with a discussion of a convenient thermodynamic indicator — the operating region.

Operating Regions

The term "operating region" does not describe a physical location, but more a "where" with respect to system operating conditions. It is a numerical value assigned to a certain reaction occurring in a given atmosphere at a given temperature. Operating regions can be calculated by substituting steady-state gas partial pressures into the usual equilibrium-constant equation:

$$\text{Operating Region} = \log \frac{(\text{Partial Pressures of Product Gases})}{(\text{Partial Pressures of Reactant Gases})}$$

This value can be used to determine the direction that the reaction should go by comparing it with the equilibrium constant for that reaction. By completing this type of analysis on the numerous reactions considered likely to occur in any one reaction unit, the thermodynamically stable form of trace and minor constituents can be determined.

Several examples of operating region calculations and analyses are presented in the section "Variability of Operating Conditions," and Appendixes D, E, and F.

Pretreatment

The reactions occurring in the pretreater are primarily oxidation devolatilization, and polymerization reactions. Several oxidation reactions were evaluated at 700 K and atmospheric pressure for sulfate, sulfite, and oxide stability. In general, the oxidation reactions strongly favor sulfate, oxide, or carbonate formation, such as —

$$MS + 2O_2 \rightleftarrows MSO_4$$
$$MS + 3/2\ O_2 \rightleftarrows MO + SO_2$$
$$MO + CO_2 \rightleftarrows MCO_3$$

As the calculations progressed, it was assumed that the sulfate or oxide form of each element would be thermodynamically favored in the pretreater. This mild oxidation is required to drive off volatile matter and to char the surface of each coal particle slightly to reduce agglomeration. The quantity of off-gases produced during pretreatment is considerable at 5728.5 g-mol/s (157.4 kg/s), (Refer to Table 1, Column D). Nitrogen and water vapor account for 85 mol % of the off-gases; carbon monoxide and carbon dioxide comprise 10 mol %. Methane, ethane, oxygen, sulfur dioxide, argon, and heavier hydrocarbons make up the remainder of an essentially neutral reaction atmosphere.

Steam Plant

The pretreater off-gases, combined with pretreater tars, oils, and fines, supplement the fuel to the steam plant. The total quantity of steam-plant feed (i.e., off-gases, oil, tars, fines, and coal) amounts to ~194 kg/s for bituminous coals. Because pretreatment is not required for nonagglomerating coals, the steam-plant fuel supplement is correspondingly reduced. The quantity of coal used for steam production is approximately 30% of the coal conveyed to the hydrogasifier.

The combustion gases from a steam plant are scrubbed to reduce sulfur dioxide emissions to acceptable levels. It is, however, uncertain that the SO_2 scrubber could completely eliminate the emission of the more volatile trace elements and this question must be resolved by actual sampling and analysis of the combustion gases.

Even though this project is directed toward evaluating the process streams of a HYGAS-based facility, consideration of the plant's auxiliary units should be made with respect to potential pollutants. Larger stack gas cleaning measures may have to be used on the steam plant, for example, depending upon the quantity of sulfur in the coal being used.

Hydrogasification

The highly reducing atmosphere of the HYGAS unit, as well as the high pressure and temperature, must be considered in determining the stable element forms. Some of the reactions that were considered likely to occur in the hydrogasifier are included here:

$$\begin{aligned}
&MO + 2HCl &&\rightleftarrows MCl_2 + H_2O\\
&MO + 2HF &&\rightleftarrows MF_2 + H_2O\\
&MO + CO_2 &&\rightleftarrows MCO_3\\
&MO + H_2S &&\rightleftarrows MS + H_2O\\
&MS + 2HCl &&\rightleftarrows MCl_2 + H_2S\\
&MS + 2HF &&\rightleftarrows MF_2 + H_2S\\
&MS + H_2O + CO_2 &&\rightleftarrows MCO_3 + H_2S\\
&MSO_4 + 4H_2 &&\rightleftarrows MS + 4H_2O
\end{aligned}$$

In addition to these, reactions involving the elemental forms were included for the more volatile species (Appendix E, Table E-2). The free-energy changes for these reactions were calculated at a steam-oxygen gasifier temperature of $\sim$1300K (1880 °F).

CO-Shift Reaction

The purpose of the CO-shift reactor is to adjust the hydrogen-to-carbon monoxide ratio in the gas stream to about 3.1:1 prior to methanation. The cobalt-molybdenum catalyst is expected to equilibrate most materials that contact it. Thus, an oxide that is more stable thermodynamically as a sulfide will react with sulfur compounds in the gas to form the sulfide. The reactions are the same as those likely to occur in the HYGAS reactor except they are evaluated at 600K.

At this point in the process, only the most volatile trace elements are in the gas stream. Most of the fine particulate matter has been removed in the hot oil quench and the cyclone, or has been adsorbed onto the catalyst.

PROCESS STEPS

The data contained in Tables 4, 6, and 7 are the result of thermodynamic and solubility calculations to determine the fate of trace and minor elements in coal during hydrogasification. The parameters used in these calculations were taken from a design for a 3.0528 GJ/s (250 billion Btu/day) coal-gasification plant based on the HYGAS Process. The coals used in the designs are bituminous, subbituminous, and lignite.

The tables include the raw coal concentrations (in parts per million) and the calculated flow rates (in kg/s) for 38 elements in the major process streams. For clarity, the stream numbers and descriptions of these tables are related to the Figure 1 process flow diagram.

The purpose of these calculations is to direct the search for trace elements toward the process streams where they are thermodynamically, or physically, more likely to appear. For example, according to trace-element studies done at IGT, cobalt or lithium are not likely to appear beyond the hydrogasifier; hence, any extensive analysis of the wastewater from the acid-gas treatment unit for these elements may generate no useful information. With the guidelines from this present study at hand, however, one may analyze process streams for specific elements and use the information in the environmental assessment of a coal gasification plant. It should be stressed that the data extrapolated from process development unit testing are preliminary estimates of the trace element distribution and should be used cautiously, but may serve to guide a future search for trace elements in pilot plant process streams.

The data used in the thermodynamic calculations were taken from a number of references.[5,17,21-23,26,27,42,53,61,63,64] Where data on a certain compound were available from two or more references, generally the data from the more recently published source were selected. Data from one reference were used with data from another as infrequently as possible, because of standard-state definition inconsistencies. If data were not available, approximations were made based on the thermodynamic properties of neighboring elements in the periodic table. The trends of the stable compounds in the hydrogasifier are outlined in Appendix C.

Table 6. CALCULATED FLOW RATES OF TRACE AND MINOR ELEMENTS IN A HYGAS-BASED, COMMERCIAL COAL-GASIFICATION PLANT USING MONTANA SUBBITUMINOUS COAL

Stream Description	Feed Coal to Slurry Feed System[a]		Oxygasifier Char	Hot Oil Quench	Water Scrub[b]	Acid-Gas Effluent[c]	Sulfur Guard	Methanation Condensate[d]	Product Gas
Stream Number	C		G	K	12, 13	11, 14	P	6	9
Element	– ppm –*	kg/s (X 10³)	kg/s (X 10³)						
Sb	1.2	0.18	0.14	0.03	0.01	0.0	0.0	0.0	0.0
As	18	2.7	1.3	0.65	0.35	0.40	0.0	0.0	0.0
Ba	1300	200.0	200.0	0.0	0.0	0.0	0.0	0.0	0.0
Be	0.98	0.145	0.113	0.032	0.0	0.0	0.0	0.0	0.0
Bi	0.72	0.11	0.06	0.045	0.005	0.0	0.0	0.0	0.0
B	85	13.0	9.05	3.5	0.45	0.0	0.0	0.0	0.0
Cd	0.72	0.11	0.05	0.048	0.012	0.0	0.0	0.0	0.0
Ca	17,000	2520.0	2520.0	0.0	0.0	0.0	0.0	0.0	0.0
Cl	180	27.0	14.1	1.0	11.9	0.0	0.0	0.0	0.0
Cr	14	2.1	1.6	0.5	0.0	0.0	0.0	0.0	0.0
Co	4.4	0.65	0.65	0.0	0.0	0.0	0.0	0.0	0.0
Cu	8.8	1.3	0.92	0.38	0.0	0.0	0.0	0.0	0.0
F	71	10.5	6.7	1.0	1.8	1.0	0.0	0.0	0.0
Ge	2.7	0.4	0.3	0.03	0.03	0.03	0.01	0.0	0.0
Fe	9200	1370.0	1370.0	0.0	0.0	0.0	0.0	0.0	0.0
Pb	1.9	0.28	0.15	0.09	0.04	0.0	0.0	0.0	0.0
Li	5.8	0.86	0.86	0.0	0.0	0.0	0.0	0.0	0.0
Mg	5800	860.0	844.0	110	5.0	0.0	0.0	0.0	0.0
Mn	8.9	1.32	1.26	0.06	0.00	0.0	0.0	0.0	0.0
Hg	0.73	0.11	0.0011	0.048	0.035	.024	0.0019	0.0	0.0
Mo	2.1	0.31	0.28	0.03	0.0	0.0	0.0	0.0	0.0
Ni	23	3.4	3.1	0.3	0.0	0.0	0.0	0.0	0.0
N	9200	1370.0	223.0	77.0	101.00	50.0	9.0	1.0	0.0
K	340	50.0	49.0	1.0	0.0	0.0	0.0	0.0	0.0
Sm	0.51	0.076	0.074	0.002	0.0	0.0	0.0	0.0	0.0
Se	1.7	0.25	0.09	0.03	0.07	0.06	0.0	0.0	0.0

* Parts per million

Table 6, Cont. CALCULATED FLOW RATES OF TRACE AND MINOR ELEMENTS IN A HYGAS-BASED, COMMERCIAL COAL-GASIFICATION PLANT USING MONTANA SUBBITUMINOUS COAL

Stream Description	Feed Coal to Slurry Feed System[a]		Oxygasifier Char	Hot Oil Quench	Water Scrub[b]	Acid-Gas Effluent[c]	Sulfur Guard	Methanation Condensate[d]	Product Gas
Stream Number	C		G	K	12, 13	11, 14	P	6	9
Element	– ppm –	kg/s (X 10^3)	kg/s (X 10^3)						
Si	13,000	1930.0	1780.0	150	0.0	0.0	0.0	0.0	0.0
Ag	0.24	0.036	0.034	0.0015	0.0005	0.0	0.0	0.0	0.0
Na	180	26.7	25.2	1.5	0.0	0.0	0.0	0.0	0.0
Sr	350	52.0	34.0	18	0.0	0.0	0.0	0.0	0.0
S	9900	1470.0	490.0	58.0	86.0	831.0	5.0	0.0	0.0
Te	0.42	0.062	0.036	0.023	0.002	0.001	0.0	0.0	0.0
Sn	1.9	0.28	0.27	0.27	0.01	0.0	0.0	0.0	0.0
Ti	320	48.0	48.0	0.0	0.0	0.0	0.0	0.0	0.0
V	67	10.0	8.0	1.7	0.3	0.0	0.0	0.0	0.0
Yb	0.36	0.053	0.047	0.004	0.002	0.0	0.0	0.0	0.0
Zn	13	1.9	1.4	0.42	0.08	0.0	0.0	0.0	0.0
Zr	25	3.7	3.3	0.4	0.0	0.0	0.0	0.0	0.0

[a] Nonagglomerating coals do not require pretreatment.

[b] Two streams are split here: The oil stream is recycled to the slurry preparation and may accumulate trace elements. The water stream contains phenols, $NH_4(F, Cl)$ to be separated, and the treated water to be recycled. It is important to note that the by-products may showenrichment of some trace elements.

[c] The sour gas from the acid-gas treatment unit is sent to the Claus plant. It contains much of the acidic compounds of CO_2, H_2S, As_2O_3, B_2O_3, etc., and fine particulates. Oil is separated during regeneration and is recycled. CO_2 is released to the atmosphere with trace sulfur compounds. Some gaseous, acidic elements, i.e., H_2Se and H_2Te, will most likely end up in the Claus plant sulfur product.

[d] Water is condensed during methanation and may carry away other trace elements. Almost total sulfur removal is accomplished during methanation by adsorption onto the catalyst particles. The product gas will be analyzed for the more volatile, toxic elements, but not for the innocuous ones.

Table 7. CALCULATED FLOW RATES OF TRACE AND MINOR ELEMENTS IN A HYGAS-BASED, COMMERCIAL COAL-GASIFICATION PLANT USING MONTANA LIGNITE

Stream Description	Feed Coal to Slurry Feed System[a]		Oxygasifier Char	Hot Oil Quench	Water Scrub[b]	Acid-Gas Effluent[c]	Sulfur Guard	Methanation Condensate[d]	Product Gas
Stream Number	C		G	K	12, 13	11, 14	P	6	9
Element	ppm*	kg/s (X 10^3)	kg/s (X 10^3)						
Sb	1.2	0.21	0.16	0.04	0.01	0.0	0.0	0.0	0.0
As	18	3.2	1.5	0.79	0.42	0.49	0.0	0.0	0.0
Ba	1300	230.0	230.0	0.0	0.0	0.0	0.0	0.0	0.0
Be	0.98	0.17	0.13	0.04	0.0	0.0	0.0	0.0	0.0
Bi	0.72	0.13	0.073	0.051	0.006	0.0	0.0	0.0	0.0
B	85	15.1	10.8	3.8	0.5	0.0	0.0	0.0	0.0
Cd	0.72	0.13	0.06	0.056	0.014	0.0	0.0	0.0	0.0
Ca	17,000	3010.0	3010.0	0.0	0.0	0.0	0.0	0.0	0.0
Cl	180	32.0	16.8	1.0	14.2	0.0	0.0	0.0	0.0
Cr	14	2.5	1.9	0.6	0.0	0.0	0.0	0.0	0.0
Co	4.4	0.78	0.78	0.0	0.0	0.0	0.0	0.0	0.0
Cu	8.8	1.6	1.1	0.5	0.0	0.0	0.0	0.0	0.0
F	71	12.6	8.0	1.5	1.6	1.5	0.0	0.0	0.0
Ge	2.7	0.48	0.37	0.04	0.03	0.03	0.01	0.0	0.0
Fe	9200	1630.0	1630.0	0.0	0.0	0.0	0.0	0.0	0.0
Pb	1.9	0.34	0.18	0.11	0.05	0.00	0.0	0.0	0.0
Li	5.8	1.03	1.03	0.0	0.0	0.0	0.0	0.0	0.0
Mg	5800	1030.0	1010.0	14.0	6.0	0.0	0.0	0.0	0.0
Mn	8.9	1.6	1.5	0.1	0.0	0.0	0.0	0.0	0.0
Hg	0.73	0.13	0.0013	0.057	0.043	0.028	0.007	0.0	0.0
Mo	2.1	0.37	0.33	0.04	0.0	0.0	0.0	0.0	0.0
Ni	23	4.1	3.7	0.4	0.0	0.0	0.0	0.0	0.0
N	9200	1630.0	266.0	92.0	1200.0	60.0	11.0	1.0	0.0
K	340	60.2	58.4	0.8	0.0	0.0	0.0	0.0	0.0
Sm	0.51	0.0903	0.089	0.0013	0.0	0.0	0.0	0.0	0.0

* Parts per million

Table 7, Cont. CALCULATED FLOW RATES OF TRACE AND MINOR ELEMENTS IN A HYGAS-BASED, COMMERCIAL COAL-GASIFICATION PLANT USING MONTANA LIGNITE

Stream Description	Feed Coal to Slurry Feed System[a]		Oxygasifier Char	Hot Oil Quench	Water Scrub[b]	Acid-Gas Effluent[c]	Sulfur Guard	Methanation Condensate[d]	Product Gas
Stream Number	C		G	K	12, 13	11, 14	P	6	9
Element	ppm	kg/s (X 10³)	kg/s (X 10³)						
Se	1.7	0.3	0.1	0.04	0.08	0.08	0.0	0.0	0.0
Si	13,000	2300.0	2125.0	175.0	0.0	0.0	0.0	0.0	0.0
Ag	0.24	0.043	0.041	0.0015	0.0005	0.0	0.0	0.0	0.0
Na	180	31.9	30.1	1.8	0.0	0.0	0.0	0.0	0.0
Sr	350	62.0	40.7	21.3	0.0	0.0	0.0	0.0	0.0
S	9900	1750.0	584.0	70.0	100.0	990.0	6.0	0.0	0.0
Te	0.42	0.074	0.042	0.027	0.003	0.002	0.0	0.0	0.0
Sn	1.9	0.34	0.32	0.02	0.0	0.0	0.0	0.0	0.0
Ti	320	57.0	57.0	0.0	0.0	0.0	0.0	0.0	0.0
V	67	12.0	9.6	2.0	0.4	0.0	0.0	0.0	0.0
Yb	0.36	0.064	0.057	0.0045	0.0025	0.0	0.0	0.0	0.0
Zn	13	2.3	1.7	0.51	0.09	0.0	0.0	0.0	0.0
Zr	25	4.4	3.9	0.5	0.0	0.0	0.0	0.0	0.0

[a] Nonagglomerating coals do not require pretreatment.

[b] Two streams are split here: The oil stream is recycled to the slurry preparation and may accumulate trace elements. The water stream contains phenols, NH_4 (F, Cl) to be separated, and the treated water to be recycled. It is important to note that the by-products may show enrichment of some trace elements.

[c] The sour gas from the acid-gas treatment unit is sent to the Claus plant. It contains much of the acidic compounds of CO_2, H_2S, As_2O_3, B_2O_3, etc., and fine particulates. Oil is separated during regeneration and is recycled. CO_2 is released to the atmosphere with trace sulfur compounds. Some gaseous, acidic elements, i.e., H_2Se and H_2Te, will most likely end up in the Claus plant sulfur products.

[d] Water is condensed during methanation and may carry away other trace elements. Almost total sulfur removal is accomplished during methanation by adsorption onto the catalyst particles. The product gas will be analyzed for the more volatile, toxic elements, but not for the innocuous ones.

The term "trace element" usually applies to concentrations of 1000 ppm or less. Minor elements occur in quantities from 1000 ppm (0.1%) to several percent. The major constituents in coal are those typically included in the ultimate analysis — carbon, hydrogen, oxygen, nitrogen, sulfur, and ash. Because of its environmental importance and ubiquity in coal, sulfur is considered a major component, though its concentration can vary from low to several percent.

The concentration of the trace and minor elements listed in Tables 4 and 7 were determined at IGT from composite samples of the two coals. The information in Table 6 was approximated from the data in Table 7. The data represent average values; however, a literature survey of the extent of trace elements in coals has shown a concentration range of about ± 1 order of magnitude. Thus, depending upon the coal source, the concentration of the trace elements may be about 10 times more or less than what is recorded here. Relative to their crustal abundance, or "clarke" value, only boron, cadmium, and selenium are enriched in coal, while fluorine, manganese, and phosphorus are at lower levels.

The question of trace-element accumulation in process streams becomes more complex and obscured beyond the severe partitioning effects (volatile element-refractory element segregation) of the hydrogasifier and steam-oxygen gasifier units. An example would be the levels of trace elements dissolved in the scrubbing media. As this media is reprocessed and recycled to the system, quantities of soluble elements may accumulate. When the solubility limit for a particular compound (or element) is exceeded, the excess will precipitate out and be removed as sludge material. The flow rate of a trace element may fluctuate somewhat with variations in the feed coal concentration; however, the solubility limit is the highest attainable level for the element in the recycled medium.

VARIABILITY OF OPERATING CONDITIONS

The effect of a change in operating conditions on the fate of trace elements during gasification will be dealt with in this report section. By utilizing an IGT computer program that simulates the major hydrogasifier and steam oxygen gasifier reactions, it is possible to follow trends in the raw gas composition due to variations in operating conditions without using the actual equipment. Some of the parameters which may be altered in a computer investigation include the steam/oxygen ratios, coal feed/steam ratios, the incorporation of either an electrothermal gasifier or steam-oxygen gasifier operations into the system, etc. (See Appendix B.) The benefits of this kind of analysis are obvious: Changes in operating conditions can be analyzed in a short time, fewer operators are required, considerably less expense is involved, and no materials are consumed.

The HYGAS Process normally operates at about 6985 to 8275 kN/m^2 (1000 to 1200 psia), and the high-temperature and steam-oxygen gasifiers operate at roughly 1210K and 1300K, respectively. If residence times are assumed to be constant, the other important changes that may occur in the reactor operating conditions are those of temperature and pressure.

In the computer simulations, the effects of different reactor pressures and temperatures on raw synthesis gas compositions were examined. In order to gauge what may result from any uncontrolled temperature fluctuations in the reactor, a range of ± 20% of the normal operating condition was used. Thus, as the normal operating temperature of the steam-oxygen gasifier is 1300K, the computer test values were set at extremes of 1560K and 1080K. The corresponding temperatures in the low and high-temperature reactors were obtained from the computer program. To evaluate the effects of different operating pressures, test values ranged from 9930 kN/m^2 (1440 psia, + 20%) down to 1825 kN/m^2 (265 psia, −78%).

In a commercial plant, automatic feedback (or feed forward) controls should be able to maintain a relatively close regulation of process temperature and pressure during steady-state operation. The widest range of process fluctuations will probably be experienced during the start-up sequence. As this process may continue over several days, the by-product streams from the plant should be closely monitored for unusual contaminants for the duration. In any system, a major upset may cause severe strains on the water or gas treatment facilities.

The key indicator in such a study is to what extent the operating regions, described previously, change due to alterations in reactor temperature and pressure. That is, for a change in temperature (or pressure), what magnitude of variation is observed for the values of operating region indicators — log (P_{H_2O}/P_{H_2S}), etc. These factors are the gauges by which the more stable forms of an element may be determined.

Table 8 contains the output data from computer runs on Illinois No. 6 seam bituminous coal using standard conditions but several variations of pressure and temperature. Column A presents the synthetic raw gas compositions for standard operating conditions. Column B reflects a low-pressure, high-temperature variation. Column C shows high-pressure, high-temperature output. When a low-pressure, low-temperature simulation was attempted, however, the computer rejected the set of conditions. The temperature was obviously too low to sustain the gasifier reactions. Columns D, E, and F are standard temperature runs with low-pressure variations. Column G contains output for a standard condition run for Montana subbituminous coal. The final column (H) contains the calculated raw gas composition using a lignite coal.

As the data of Table 8 indicate, the raw gas compositions vary considerably with changing operating conditions for the same coal. Yet if one compares several examples and calculates the values for the operating regions, the variations do not represent major changes in the thermodynamic driving force. This is shown in the tabulation given below. The figures are based on calculations using the Ideal Gas Law and carry some uncertainty.

In the examples using Illinois No. 6 bituminous coal, the H_2S concentration ranges from a low of 0.89 mol% (Column A, steam-oxygen gasifier) to 1.30 mol% (Column D, electrothermal gasifier). Depending upon the reaction thermodynamics, this difference may or may not affect the ultimate form of the element in a changing system. Consider these two typical gas-phase (heterogenous) reactions.

$$MO(s) + H_2(g) \rightleftarrows M(s) + H_2O\,(g), \log K_{eq} = 2.0 \quad (1)$$

$$MO(s) + H_2S(g) \rightleftarrows MS(s) + H_2O(g), \log K_{eq} = 1.2 \quad (2)$$

Table 8. COMPUTER-CALCULATED COMPOSITION OF HYGAS REACTOR RAW SYNTHESIS GAS FOR VARIOUS TEMPERATURES AND PRESSURES

	A Standard Temperature, Pressure[d]	B High Temperature,[d] Low Pressure	C High Temperature, Pressure	D Standard Temperature, Low Pressure	E Standard Temperature, Low Pressure	F Standard Temperature, Low Pressure	G Standard Temperature, Pressure	H Standard Temperature, Pressure
Coal Type	Illinois No. 6 Bituminous					Pittsburgh Bituminous	Montana[b] Subbituminous	Lignite
Component	mol %							
CO	19.45	21.63	19.89	31.72	23.93	19.92	14.21	12.89
CO_2	20.09	18.92	20.17	6.95	15.94	17.70	20.31	19.49
H_2	21.01	25.63	22.68	39.09	28.32	24.38	19.85	22.14
H_2O	22.98	23.59	24.28	9.08	19.92	22.97	30.18	35.39
CH_4	14.88	8.62	11.34	9.99	9.71	12.83	13.26	8.89
C_2H_6	0.28	0.26	0.27	0.76	0.52	0.52	1.03	0.40
C_6H_6	0.09	0.08	0.08	0.25	0.17	0.17	0.16	0.20
NH_3	0.33	0.30	0.31	0.58	0.39	0.40	0.38	0.40
H_2S	0.89	0.97	0.98	1.30	0.90	0.90	0.22	0.20
N_2	0.00	0.00	0.00	0.05	0.03	0.04	0.03	—
	100.00	100.00	100.00	99.77[a]	99.83[a]	99.83[a]	99.63[a]	100.00
Operating Conditions								
Low-Temperature Reactor, K	950	1140	1140	880	965	970	900	950
High-Temperature Reactor, K	1210	1450	1450	1228	1210	1210	1200	1210
Oxygasifier, K	1300	1530	1530	1310[c]	1300	1300	1300	1300
Pressure, kN/m²	8275 (1200 psia)	6618 (960 psia)	9930 (1440 psia)	1825 (265 psia)	3620 (525 psia)	5620 (815 psia)	8065 (1170 psia)	6895 (1000 psia)

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[a] Includes small quantity of new oil make material.

[b] Sulfur content, 0.66%; moisture, 22.0%.

[c] Electro-thermal gasifier.

[d] The terms standard temperature or standard pressure refer to the operating conditions in the steam-oxygen gasifier. Standard temperature is 1300K (1880°F) and standard pressure is 8275 kN/m² (1200 psia) in the steam-oxygen gasifier.

The corresponding temperatures of the low-and high- temperature reactors were obtained from the computer program.

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Operating Conditions	A Standard Temperature, Pressure	B High T, Low P	C High T, High P	D Standard T, Low P
Temperature, K	1300	1530	1530	1310*
Pressure, kN/m²	8275	6620	9930	1825
(psia)	(1200)	(960)	(1440)	(265)
Operating Regions				
(1) $\log[P_{H_2O}/P_{H_2}]$	0.04	−0.04	0.03	−0.63
(2) $\log[P_{H_2O}/P_{H_2S}]$	1.41	1.39	1.39	0.84

*Electrothermal gasifier.

Note that the numerical difference between log K_{eq} (2.0) and the Operating Region (see above values), which is the thermodynamic driving force for Equation 1 may be from 1.96 (Column A) to 2.63 (Column D). The driving force does not undergo a sign change, nor a significant change in magnitude, thus the expected product for this reaction is M (s).

For Equation 2, the thermodynamic driving force ranges from −0.21 (Column A) to 0.36 (Column D). Thus, for a situation in which a gasifier loses significant system pressure (while maintaining temperature), the new steady-state operating conditions may cause a reversal of the driving force. The raw synthesis gas composition would change from the one listed in Column A (Table 8) to the one listed in Column D (Table 8), with a corresponding change in operating regions. If the magnitude of the driving force (i.e., log K_{eq} − Operating Region) is near zero, the ratio of products to reactants at steady-state will remain unchanged.

Further calculations must be made in order to determine other possible reactions which may form chlorides or hydrides, for example. In general, it is not expected that altering the temperature and pressure of this system would change the final distribution of the trace elements significantly. Some of the minor elements such as nitrogen and sulfur, show variations in flow quantities which may be of concern downstream during operation of the purification system.

The assumption of constant residence times is not strictly valid across the temperature and pressure range discussed. An investigation to determine the effects of prolonged residence times on trace-elements' volatilization should be undertaken. It is likely that some trace-element losses may be proportional to residence time.

The temperatures which have been used in the computer analyses are averages over the entire fluidized reactor bed volume. They do not address the possibility that localized hot spots may exist in the steam-oxygen gasifier, above the oxygen sparger. These hot spots may be several hundred degrees hotter than the surrounding areas and thus, enhance the volatilization of some, otherwise refractory trace elements. The effects of these hot spots on trace-element distribution are not well understood and may be significant. Further investigation is necessary.

SAMPLING

Sampling Points

The sampling points described in Table 9 and shown in Figure 2 refer to locations at the HYGAS pilot plant that will yield the most useful information concerning trace-element distribution in a commercial-size coal gasification plant. It must be emphasized, however, that significant calculations and engineering estimates must be made in order to extrapolate from pilot- to commercial plant-scale.

Table 9 includes actual, operational data on the temperature, pressure, and flow rates of the pilot-plant process streams. The type of sample required at each location is indicated to the right of the listing. Figure 2 identifies each sampling point with respect to other process units and also gives the concurrent phase or phases to be sampled. In this test plan, some typical solid-waste streams are to be sampled as slurries (SL) for both solid and liquid phases. The high pressures encountered in the HYGAS Process require that all solid streams be slurried with water prior to discharge. Thus, the material sampled from the primary cyclone (Sample Location 4) will include the effluent slurry medium (L) as well as the particulate matter (S). Care must be taken during sampling and analysis, to account for water soluble constituents of slurry discharge as well as the constituents contained in the solid residues.

Similarly, typical liquid effluent streams will be tested for particulate matter, which may accompany the liquid by entrainment or by incomplete phase separations. The product gas stream (Sample Location 11) will be sampled to determine if any of the more volatile trace elements have survived the numerous gas-cleaning steps. The pretreater (Sample Location 12) produces solid, liquid, and gaseous effluents. This stream is expected to harbor much of the more toxic, volatile elements; hence, their analyses should be of considerable interest.

The base-line data points for the quench water, and toluene washes should be established early in the test program, as some trace elements may tend to accumulate in the reactor through a volatilization,

Table 9. HYGAS PILOT PLANT SAMPLING POINTS

Sample Description	Sample Phase
1. Raw Coal Ambient Conditions	Solid
2. Pretreated Coal (char) 0.75 kg/s (6000 lb/hr) 700°K (800°F) 115 kN/m^2 (2 psig)	Solid
3. Light Oil (Toluene) 2.268 kg/s, (18,000 lb/hr) Ambient Temp, Pressure	Liquid
4. Cyclone Fines 0.126 kg/s (1000 lb/hr) 645°K (700°F) 6895 kN/m^2 (1000 psia)	Slurry
5. Ash From Oxygen Gasifier 0.1327 kg/s (1053 lb/hr) 1090°K (1500°F) 6930 kN/m^2 (1005 psia)	Slurry
6. Char Slurry From Prequench Tower 0.52 kg/s (4140 lb/hr) 408°K (275°F) 6865 kN/m^2 (996 psia)	Slurry
7. Quench Water to Quench Tower 7.938 kg/s (63000 lb/hr) 310°K (99°F) 6825 kN/m^2 (990 psia)	Liquid
8. Net Toluene to Storage 2.261 kg/s (17944 lb/hr) 315°K (110°F) 6825 kN/m^2 (990 psia)	Liquid, Solid
9. Water Scrub Influent (Base) Water Scrub Effluent	Liquid Liquid, Solid
10. Acid Gas From Acid-Gas Treatment 0.383 kg/s (3039 lb/hr) 333°K (140°F) 117 kN/m^2 (17 psia)	Gaseous
11. Product-Gas Stream 0.0693 kg/s (550 lb/hr) 310°K (100°F) 6275 kN/m^2 (910 psia)	Gaseous
12. Pretreatment Off-Gases, Tars, Oils Ambient Conditions	Solid, Liquid, Gaseous

condensation, and revolatilization process. A similar recycling of trace elements may occur in the slurry system. The levels of these accumulations should be measured periodically in the sampling program to determine if steady-state levels are attained.

The distribution of certain elements, such as nickel or vanadium, that may plate out on process-unit walls, could be estimated more closely by positioning test coupons in the process gases. However, such a procedure would be somewhat academic, as both vanadium and nickel should appear in the ash or in the entrained particulates from the quench towers, thus reducing the pollution concern.

The pilot plant is, of course, not of commercial size; its capacity is roughly 0.78 kg/s (75 tons/day). Not all of the process units required in a commercial plant are in operation at present. As the by-product recovery units come on-stream, however, the analysis of trace elements can be extended to include each by-product. Much will be revealed about the efficiency of the recovery units as well as the salability of the by-product itself.

Not all of the HYGAS pilot-plant process units relate directly to the example of a HYGAS-based commercial design, as presented in Figure 1. For example, the pilot plant utilizes a prequench tower prior to quenching, and the quench liquor is water rather than a cool oil. The cyclone fines are discarded at present and not recycled as they would be in the proposed commercial plant. The steam plant at the pilot plant is gas-fired, not coal-fired, as presented.

The levels of trace constituents in each of the process streams can be determined from the data of Tables 4, 6, and 7. Since the flow rates of these tables are based on a commercial-sized coal facility, each must be scaled down to correlate with the lower flow rates of the pilot plant. Depending upon the feed coal, the capacity of the HYGAS pilot plant is from 233 to 346 times less than the corresponding commercial-size plant. (See Appendix C for the basis of these factors.)

With scaling factors of such magnitude, it is imperative that each sample taken be representative of the lot,and that sufficient numbers of samples be analyzed to ensure that the results have statistical significance.

To maintain sample consistency, standard methods of solid, liquid, and gaseous sampling have been selected from ASTM procedures. Statistically significant results will be attained by sampling each location frequently (≧ 20 times) over the course of a 7-day, steady-state, performance-evaluation period.

Sampling Techniques

Solid Samples

These include both dry, solid discharges and water-slurried, solid discharges. Each will be collected and prepared according to ASTM Methods, D-2234-72, "Sampling of Coal" and D-2013-72, "Preparing Coal for Analyses," respectively.

Liquid Samples

An integral part of the liquid-sampling plan is to obtain flow information on various in-plant streams as well as on the plant outfall to facilitate completion of the following tasks:

> The characterization of flow rates of waste water and other liquid effluents as well as variations in them caused by process upsets
>
> The determination of the total amounts of each constituent emitted from each stream based on the analytical data and the determined flow rate
>
> The calculation of the solid and liquid mass balances based on the analytical data gathered for these two kinds of sample analyses

Process stream flow rates can be approximated by the following methods: 1) water meters on effluent lines, 2) container and stopwatch, and 3) salt concentration. The details of these and alternative measuring methods can be found in many references.[65,66] One or more of them should be used in conjunction with operating parameters available from HYGAS pilot-plant records.

Some analytical parameters of the liquid sample, such as the pH and temperature, should be measured at the time of sampling. Other analytical tests require that the sample be chemically fixed immediately after collection. This is done to reduce the degradation of certain organic or inorganic constituents in the sample, which may occur during shipping and storage. Common analytical determinations that require special sample fixation, their maximum holding time before chemical analyses, and the proper types of containers for collection, are given in Table 10. Separate samples are needed for analytical tests, which require that the sample be fixed with different preservatives.

Gaseous Samples

Gaseous sampling systems will be set up following the ASTM atmosphere-sampling method. "Standard Recommended Practices for Sampling Atmosphere for Analysis of Gases and Vapors," D-1605, Part 23, and the "Standard Method for Sampling Stacks for Particulate Matter," D-2928, Part 23 — ASTM standard methods — will be correlated into one sampling system.

The particulate matter will be collected on a 47-mm filter, and the gases and the vapors passing through the filter will be collected in a freeze-out sampling train consisting of a series of traps at progressively lower temperatures. The refrigerant should be sufficiently cold to ensure that the vapor pressure of any trapped material will be low enough to prevent significant evaporation during the sampling.

Table 10. PARAMETERS RELATING TO PRESERVATION, HOLDING TIME, AND SAMPLE STORAGE

Holding Time	Parameter	Preservation	Container
None	pH		
	Temperature		
6-12 hr	BOD_5*	Refrigeration, 4°C	Glass or plastic
	Mercury	None	Glass or PVC
	Nitrogen (Total)	40 mg $HgCl_2/\ell$ refrigeration, 4°C	
24 hr	Color	Refrigeration, 4°C	Glass
	Cyanide	NaOH to $pH > 10$	Glass or plastic
	Oil and grease	2 ml H_2SO_4/ℓ refrigeration, 4°C	Glass
	Phenolics	1 g $CuSO_4/\ell$ H_3PO_4 to pH 4	Glass
	Odor	Refrigeration, 4°C	Glass
7 days	Calcium	None required	Plastic or glass
	TOC*	2 ml H_2SO_4 (or HCl) to pH 2	Plastic or glass
	COD*	2 ml H_2SO_4	Plastic or glass
	Fluoride	None required	Plastic or glass
	Hardness	None required	Plastic or glass
	Nitrogen (NH_3)	40 mg $HgCl_2/\ell$, refrigeration, 4°C	Plastic or glass
	Nitrogen NO_3, NO_2	40 mg $HgCl_2/\ell$, refrigeration, 4°C	Plastic or glass
	Phosphorus	40 mg $HgCl_2/\ell$, refrigeration, 4°C	Plastic or glass
	Solids	None required	Plastic or glass
	Sulfate	Refrigeration, 4°C	Plastic or glass
	Sulfide	2 ml Zn acetate/ℓ	Plastic or glass
	Turbidity	None available	Plastic or glass
6 months	Metals	5 ml HNO_3/ℓ	Glass

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* BOD_5 is 5-day biological oxygen demand.

TOC is total organic carbon.

COD is chemical oxygen demand.

ANALYTICAL METHODS

Solid Samples

These samples include raw and pretreated coal, coal fines, slurry solids, and solid by-products. They should be analyzed for trace and minor constituents. The initial step for most trace-element analysis is ashing of the solid sample in a low-temperature ash (LTA) plasma machine, with subsequent dissolution in the proper acid mixture. Due to volatility, some elements (such as mercury) will be lost during the LTA process. As a result, a duplicate sample will be needed for analysis by an appropriate analtyical scheme.

The analytical methods to be used for each elemental analysis and some possible alternative methods are given in Table 11. The actual analytical technique to be used for the determination of each constituent will depend upon the level of that element in the sample as well as on the possible interferences due to the presence of other elements. A NBS standard reference coal sample should be concurrently analyzed to ensure the accuracy of the analyses.

Liquid Samples

These samples include any process unit tars and oils, quench liquor, toluene, recycled waste water, phenols, and ammonia. Some liquid samples will contain large quantities of solids and organic materials. Aqueous samples should be tested for BOD_5, COD, color, oil and grease, TOC, TS, TDS, TSS, and turbidity in the whole sample.* Organic samples need to be analyzed for trace elements and organic constituents, specifically polynuclear

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* BOD_5 is the 5-day biological oxygen demand.
COD is the chemical oxygen demand.
TOC is total organic carbon.
TS is total solids.
TDS is total dissolved solids.
TSS is total suspended solids.

Table 11, Part 1. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent	Method	Detection Limit[b]	Range[c]	Precision, %[d]
Antimony	1. LTA-acid dissolution[a] Iodide-benzene extraction Flameless AAS	0.001 ppm	0.04-2 ppm	5
	2. LTA-acid dissolution[a] Hydride formation Heated-quartz-cell AAS	0.001 ppm		3
Arsenic	1. LTA-acid dissolution[a] Flameless AAS	0.01 ppm	3.0-30 ppm	7
	2. LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Air-C_2H_2 flame AAS	0.05 ppm		5
	3. LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Flameless AAS	0.001 ppm		7
	4. LTA-acid dissolution[a] Hydride formation Heated-quartz-cell AAS	0.001 ppm		3
Barium	1. HTA-acid dissolution[a] $N_2O-C_2H_2$ FES	0.01 ppm	20 ppm – 2%	5
	2. HTA-acid dissolution[a] H_2SO_4 ppt NH_4OH-EDTA redissolution $N_2O-C_2H_2$ FES	0.001 ppm		4
	3. HTA-Na_2CO_3 fusion[65] Hot-water leaching HCl dissolution $N_2O-C_2H_2$ FES	0.001 ppm		4
Beryllium	1. LTA-acid dissolution[a] $N_2O-C_2H_2$ AAS	0.002 ppm	0.2-2 ppm	7
	2. LTA-acid dissolution[a] Flameless AAS	0.0001 ppm		5
Bismuth	LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.02 ppm	0.2-2 ppm	5

Table 11, Part 2. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent	Method	Detection Limit[b]	Range[c]	Precision, %[d]
Boron	LTA-Na_2CO_3 fusion[a] Diol-$CHCl_3$ extraction N_2O-C_2H_2 FES	0.05 ppm	30-500 ppm	5
Cadmium	1. LTA-acid dissolution[a] APCD-MIBK extraction Air-C_2H_2 flame AAS	0.005 ppm	0.1-10 ppm	4
	2. LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.0001 ppm	1-50 ppm	5
Calcium	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.002 ppm	0.1%-2%	3
Chlorine	Eshka-HNO_3 extraction[65] Amperonietric titration	1 ppm	0.01% ~ 0.5%	8
Chromium	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	10-500 ppm	4
Cobalt	1. LTA-acid dissolution[a] Flameless AAS	0.001 ppm	1-50 ppm	5
	2. LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.0001 ppm		6
Copper	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	5-50 ppm	3
Fluorine	Oxygen Bomb — SIE[a]	0.1 ppm	30-300 ppm	9
Germanium	LTA-emission spectrography	1 ppm	1-40 ppm	10
Iron	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.005 ppm	0.2% ~ 5%	2
Lead	1. LTA-acid dissolution[a] APCD-MIBK extraction Air-C_2H_2 flame AAS	0.01 ppm	2-50 ppm	4
	2. LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.001 ppm		6
Lithium	LTA-acid dissolution[a] N_2O-C_2H_2 FES	0.001 ppm	2-50 ppm	3

Table 11, Part 3. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent	Method	Detection Limit[b]	Range[c]	Precision, %[d]
Magnesium	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.001 ppm	0.02% ~ 1%	2
Manganese	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	5-100 ppm	3
Mercury	Total combustion – $KMnO_4$[a] Cold vapor flameless AAS	0.1 ppb	0.01-5 ppm	10
Molybdenum	LTA-acid dissolution[a] Flameless AAS	0.005 ppm	1-10 ppm	6
Nickel	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	10-50 ppm	4
Nitrogen	Kjeldahl digestion – titration[1]			
Potassium	LTA-acid dissolution[a] Air-C_2H_2 FES	0.001 ppm	0.02%-0.2%	3
Samarium	LTA-emission spectrography[a]	0.5 ppm	0.2-2 ppm	10
Selenium	1. LTA-acid dissolution[a] Flameless AAS	0.01 ppm	0.1-50 ppm	6
	2. LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Flameless AAS	0.001 ppm		5
Silicon	1. LTA-gravimetric method[a]	0.1 mg	1%-5%	2
	2. LTA-acid digestion bomb[a] N_2O-C_2H_2 flame AAS	0.1 ppm		3
Silver	LTA-acid dissolution[a] Flameless AAS	0.001 ppm	0.1-5 ppm	6
Sodium	LTA-acid dissolution[a] Air-C_2H_2 FES	0.005 ppm	0.01 ~ 0.2 ppm	3

Table 11, Part 4. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent		Method	Detection Limit[b]	Range[c]	Precision, %[d]
Strontium		LTA-acid dissolution[a] N_2O-C_2H_2 FES	0.001 ppm	10-500 ppm	3
Sulfur		Eshka-gravimetric method[1]	0.1 mg	0.1% ~ 5%	2
Tellurium	1.	LTA-acid dissolution[a] Flameless AAS	0.01 ppm	0.1 ~ 10 ppm	6
	2.	LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Flameless AAS	0.001 ppm		5
Thorium		LTA-acid dissolution[a] Ion-exchange column separation Colorimetric method	0.02 ppm	0.1 ~ 5 ppm	6
Tin	1.	LTA-acid dissolution[a] Iodide-isopropyl/ ether extraction Flameless AAS	0.01 ppm	0.1 ~ 5 ppm	6
	2.	LTA-acid dissolution[a] Hydride formation Heated-quartz-cell AAS	0.01 ppm		5
Titanium		LTA-acid dissolution[a] N_2O-C_2H_2 flame AAS	0.1 ppm	0.01% ~ 0.1%	4
Vanadium	1.	LTA-acid dissolution[a] N_2O-C_2H_2 flame AAS	0.2 ppm	10-100 ppm	10
	2.	LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction N_2O-C_2H_2 flame AAS	0.01 ppm		5
Ytterbium		LTA-emission spectrography[a]	0.1 ppm	0.1-1 ppm	10

Table 11, Part 5. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent	Method	Detection Limit[b]	Range[c]	Presicion, %[d]
Zinc	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	5-100 ppm	6
Zirconium	LTA-emission spectrography[a]	1 ppm	10-100 ppm	10

Abbreviations:

AAS — Atomic absorption spectrophotometer
APCD — Ammonium pyrrolidine carbodithioate
Diol — 2-ethyl-1, 3-hexanediol
EDTA — Ethylenediamine tetraacetic acid
FES — Flame emission spectrophotometer
HTA — High-temperature ashing
LTA — Low-temperature ashing
MIBK — Methylisobutyl ketone
SIE — Selective ion electrode.

Notes:

[a] Methods currently in use at IGT.

[b] Detection limits are estimated as the concentration of the constituent in the sample solution or mixture that would produce a signal twice as large as the background noise level. In gravimetric methods, detection limits are expressed as the minimum weight the balance can accurately weigh (0.1 mg in IGT's Analytical Laboratory).

[c] The range refers to the estimation of the constituent concentration in the sample.

[d] Precisions are estimated by applying the specified analytical method to the sample in the estimated range.

aromatics. Any emulsified samples should then be separated into three portions — organic, aqueous, and solid — by filtration and solvent extraction. The solid portion of the sample should be analyzed for trace and minor constituents and treated as any other solid sample. A measured portion of the organic phase of the sample should be evaporated carefully, wet-ashed, and also analyzed for trace elements. The aqueous portion of the sample will be analyzed for the parameters listed in Table 12. EPA reference water samples will be analyzed concurrently to ensure the accuracy of the measurements.

Gaseous Samples

The entrained particulate matter in gas should be separately recovered by filtration and analyzed for trace elements using the analytical methods for solid samples. The gases and vapors collected in the freeze-out apparatus will be combined and analyzed according to the methods given in Table 13. We expect that considerable water vapor will condense and freeze from samples taken from Sample Location No. 12, pretreater off-gases. The volumes of water can be reduced by preconcentration of the samples to render them more manageable for analysis. In addition, provisions should be made to recover and determine the concentration of polynuclear aromatics in the effluents of all the stacks in the plant.

Table 12, Part 1. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF LIQUID SAMPLES

Parameter	Method	Detection Limit[b]	Range[c]	Precision, %[d]
BOD, 5 Days	Modified Winkler or Probe Method[65,67,68]	60 ppm	NA	20
COD	Dichromate reflux[65,67,68]	50 ppm	2000 ~ 50,000 ppm	10
Chloride	Amperometrical titration[65,67,68]	1 ppm	30-500 ppm	5
Color	Platinum-cobalt visual[67,68]	--	--	--
Cyanide	1. Distillation – silver nitrate titration[65,67,68]	0.1 ppm	0.1 ~ 0.6 ppm	30
	2. Pyridine pyrazolone colorimetric[65,67,68]	0.01 ppm		4
	3. SIE	0.01 ppm		5
Mercaptans	GC – photometric detector[a]		NA	NA
Metals				
Aluminum	1. N_2O-C_2H_2 flame AAS[68]	0.1 ppm	NA	3
	2. N_2O-C_2H_2 FES[a]	0.001 ppm		2
Antimony	1. Air-C_2H_2 flame AAS	0.1 ppm	0.001	--
	2. Hydride formation[a] Heated-quartz-cell AAS	0.001 ppm	–0.005	5
Arsenic	1. Silver diethyldithiocarbonate[3]	0.01 ppm	0.028-0.044 ppm	--
	2. Air-C_2H_2 flame AAS[a]	0.1 ppm	0.01-0.1 ppm	--
	3. APCD-MIBK extraction[a] Air-C_2H_2 flame AAS	0.01 ppm		--
	4. APCD-MIBK extraction[a] Flameless AAS	0.001 ppm		5
	5. Hydride formation[a] Heated-quartz-cell AAS	.001 ppm		3
Barium	1. N_2O-C_2H_2 flame AAS[68]	0.05 ppm	0.11 ~ 0.16 ppm	30
	2. N_2O-C_2H_2 FES[a]	0.001 ppm		3

Table 12, Part 2. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF LIQUID SAMPLES

Metals	Method	Detection Limit[b]	Range[c]	Precision, %[d]
Beryllium	1. N_2O-C_2H_2 flame AAS[63]	0.002 ppm	0.001- 0.1 ppm	--
	2. Flameless AAS[a]	0.1 ppb		4
	3. Solvent extraction[a] Flamesless AAS	0.01 ppb		5
Boron	Curcumin colorimetric[67]	0.2 ug	0.05 ~ 10 ppm	5
Cadmium	1. Air-C_2H_2 flame AAS[68]	0.005 ppm	0.4 ~ 1 ppb	--
	2. Flameless AAS[a]	0.05 ppb		5
	3. APCD-MIBK extraction[a] Flameless AAS	0.005 ppb		7
Calcium	Air-C_2H_2 flame AAS[68]	0.002 ppm	3.6-4.4 ppm 10-200 ppm	3
Chromium	1. Air-C_2H_2 flame AAS[68]	0.005 ppm	NA	3
	2. Flameless AAS[a]	5 ppb		5
Cobalt	1. Air-C_2H_2 flame AAS[68]	0.005 ppm	1-2 ppb	--
	2. APCD-MIBK extraction[a] Air-C_2H_2 flame AAS	0.5 ppb		30
	3. APCD-MIBK extraction[a] Flameless AAS	0.01 ppb		6
Copper	1. Air-C_2H_2 flame AAS[68]	0.005 ppm	0.016- 0.020 ppm	20
	2. APCD-MIBK extraction[a] Air-C_2H_2 flame AAS	0.5 ppb		5
Iron	1. Air-C_2H_2 flame AAS[68]	0.005 ppm	2.6-2.9 ppm	3
	2. APCD-MIBK extraction[a] Air-C_2H_2 flame AAS	0.5 ppb		5

Table 12, Part 3. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF LIQUID SAMPLES

Metals	Method 1	Detection Limit[b]	Range[c]	Precision, %[d]
Lead	1. Air-C_2H_2 flame AAS[68]	0.03 ppm	0.01-0.1 ppm	--
	2. APCD-MIBK extraction[a] Air-C_2H_2 flame AAS	0.003 ppm		10
	3. Flameless AAS[a]	0.1 ppb		5
Fluoride	SIE	0.1 ppm		5
Germanium	1. N_2O-C_2H_2 flame AAS[68]	2 ppm	0.032 - 0.061 ppm	--
	2. N_2O-C_2H_2 FES[a]	0.5 ppm		--
	3. Hydride formation[a] Heated-quartz-cell AAS	0.005 ppm		6
Magnesium	Air-C_2H_2 flame AAS[68]	0.01 ppb	1.5-1.8 ppm	2
Mercury	Cold-vapor flameless AAS[a,68]	0.01 ppb	0.4 ~ 5ppb	5
Molybdenum	N_2O-C_2H_2 flame AAS[68]	0.05 ppm	NA	3
Nickel	1. Air-C_2H_2 flame AAS[a,68]	0.005 ppm	0.023 ~ 0.034 ppm	20
	2. APCD-MIBK extraction[a] Air-C_2H_2 flame AAS	0.05 ppb		10
Potassium	1. Air-C_2H_2 flame AAS[68]	0.005 ppm	0.1 ~ 0.2 ppm	3
	2. Air-C_2H_2 FES[65]	0.5 ppb		2
Selenium	1. Air-C_2H_2 flame AAS[68]	0.3 ppm	0.3 ~ 0.4 ppm	--
	2. Flameless AAS[65]	0.001 ppm	0.001 ~ 0.05 ppm	6
Silver	1. Air-C_2H_2 flame AAS[68]	0.005 ppm	NA	3
	2. Flameless AAS[a]	0.05 ppb		6
Sodium	1. Air-C_2H_2 flame AAS[68]	0.002 ppm	NA	3
	2. Air-C_2H_2 FES	0.05 ppb		2
Strontium	1. Air-C_2H_2 flame AAS[68]	0.01 ppm	0.024 ~ 0.033 ppm	20
	2. N_2O-C_2H_2 FES[a]	0.1 ppb		3

Table 12, Part 4. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF LIQUID SAMPLES

Metals		Method	Detection Limit[b]	Range[c]	Precision, %[d]
Tellurium	1.	Air-C_2H_2 flame AAS[68]	0.1 ppm	0.001 ~ 0.05 ppm	--
	2.	Flameless AAS[a]	0.001 ppm		8
Tin	1.	Air-C_2H_2 flame AAS[68]	0.06 ppm	0.016 - 0.020 ppm	--
	2.	Flameless AAS[a]	0.001 ppm		8
Vanadium	1.	N_2O-C_2H_2 flame AAS[a,68]	0.02 ppm	0.002 - 0.004 ppm	--
	2.	APCD-MIBK extraction[a] N_2O-C_2H_2 flame AAS	0.002 ppm		--
	3.	APCD-MIBK extraction[a] Flameless AAS	0.2 ppb		10
Zinc	1.	Air-C_2H_2 flame AAS[68]	0.002 ppm	0.044 - 0.083 ppm	8
	2.	APCD-MIBK extraction[a] Air-C_2H_2 flame AAS	0.2 ppb		6
Zirconium		N_2O-C_2H_2 flame AAS[68]	5 ppm	NA	3
Parameter					
Nitrogen (Ammonia)	1.	Distillation nesslerization[65,67,68]	0.05 ppm	2500 ~ 11,000 ppm	10
	2.	SIE[a]	0.01 ppm		4
Nitrogen (Nitrate)	1.	Brucine sulfate[65,67,68]	0.2 ppm	NA	20
	2.	SIE[a]	1 ppm		NA
Nitrogen (Nitrite)		Diazotization colorimetric[65,67,68]	0.05 ppm	NA	NA
Nitrogen (Total)		Digestion — distillation[65,67,68], and titration	0.05 ppm	NA	4
Oil and Grease		Liquid-liquid extraction[65,67,68]	0.5 mg	NA	NA

Table 12, Part 5. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF LIQUID SAMPLES

Parameter		Method	Detection Limit[b]	Range[c]	Precision, %[d]
Phenolics	1.	Colorimetric method[65,67,68]	2 ppm	200- 6600 ppm	4
	2.	GC – hydrogen flame detector[65,67,68]	1 ppm		4
	3.	GC – MS[a]	1 ppm		NA
Polynuclear Aromatics		Solvent Extraction, GC-MS	NA	NA	NA
Sulfate	1.	Turbidimetric method[65,67,68]	4 ppm	NA	6
	2.	SIE[a]	0.1 ppm		6
Sulfide	1.	Titrimetric method[65,67,68]	1 ppm	NA	NA
	2.	SIE[a]	0.01 ppm		5
Thiocyanate		Colorimetric method[a]	0.1 ppm	20-1000 ppm	5
Turbidity		Turbidimetric method[65,67,68]	1 Jackson unit	NA	NA
TS		Gravimetric, 105°C[65,67,68]	0.5 mg	NA	NA
TDS		Glass fiber filtration, 180°C[65,67,68]	1 mg	NA	NA
TSS		Glass fiber filtration, 103°-105°C[65,67,68]	1 mg	NA	NA

Abbreviations:

AAS – Atomic absorption spectrophotometer
APCD – Ammonium pyrrolidine carbodithioate
BOD – Biochemical oxygen demand
COD – Chemical oxygen demand
FES – Flame emission spectrophotometer
GC – Gas chromatography
MIBK – Methylisobutyl ketone
MS – Mass spectrometry
NA – Not available
SIE – Selective ion electrode
TDS – Total dissolved solids
TS – Total solids
TSS – Total suspended solids.

Table 12, Part 6. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF LIQUID SAMPLES

Notes:

[a] Methods currently in use at IGT.

[b] Detection limits are estimated as the concentration of the constituent in the sample solution that would produce a signal twice as large as the background noise.

[c] The range refers to the estimation of the constituent concentration in the sample solution.

[d] Precisions are estimated by applying the specified analytical method to the sample in the estimated range.

Table 13. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF GASEOUS SAMPLES

Constituent	Method	Detection Limit[a]	Range[b]	Precision, %[c]
Antimony	1. Flameless AAS	0.001 ppm	NA	5
	2. Hydride formation – Heated-quartz-cell AAS	0.001 ppm		3
Arsenic	1. APCD-MIBK extraction Flameless AAS	0.001 ppm	NA	6
	2. Hydride formation Heated-quartz-cell AAS	0.001 ppm		3
Cadmium	Flameless AAS	0.1 ppb	NA	5
Chlorine	Amperometrical titration	1 ppm		
Fluoride	SIE	0.1 ppm	NA	5
Germanium	Flameless AAS	0.01 ppm	NA	5
Hydrogen Cyanide	1. Colorimetric method	0.1 ppm	2-20 ppb	5
	2. Pyridine pyrazolone colorimetric	0.01 ppm		4
	3. SIE	0.01 ppm		5
Lead	1. Flameless AAS	0.001 ppm	NA	5
	2. APCD-MIBK extraction Flameless AAS	0.1 ppb	NA	6
Mercury	Cold-vapor flameless AAS	0.01 ppb	0.01 ppb	5
Nitrogen (NO_2)	Colorimetric method	0.5 ppm	NA	5
Phenolics	1. Colorimetric method	2 ppm	NA	4
	2. GC – hydrogen flame detector	1 ppm		4
	3. GC – MS	1 ppm		NA
Selenium	Flameless AAS	0.001 ppm	NA	6

Table 13, Cont. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF GASEOUS SAMPLES

Constituent	Method	Detection Limit[a]	Range[b]	Precision, %[c]
Sulfur (SO_2)	Conductivity method	0.1 ppm	NA	3
Sulfur (Organic)	GC – photometric detector	0	NA	--
Tellurium	Flameless AAS	0.001	NA	4
Tin	Flameless AAS	0.001	NA	4

Abbreviations:

AAS – Atomic absorption spectrophotometer
APCD – Ammonium pyrrolidine carbodithioate
GC – Gas chromatography
MIBK – Methylisobutyl ketone
MS – Mass spectrometry
NA – Not available
SIE – Selective ion electrode.

Notes:

[a] Detection limits are estimated for the specified analytical method after the sample has been put into solution.

[b] Most ranges of these parameters are not available.

[c] Precisions are estimated for each analytical method separately.

SIGNIFICANCE OF RESULTS

This research effort has been directed toward the systematic development of an environmental test plan to investigate the fate of constituents of coal and potential pollutants during gasification. The test plan is a logical and well-conceived approach to the problem of sample collection and analysis for trace elements in feeds and residues from coal gasification facilities. Both engineering and scientific contributions have been made in the development of the program. Its implementation at the HYGAS pilot plant or a similar facility will yield important information on the effluent waste streams and the efficiencies of by-product recovery units. The following discussion addresses significant areas of the engineering and analytical work that were performed during the 6-month program.

Making an estimate of the environmental impact of a new process requires a careful engineering analysis of the process streams. Descriptions of the environment in the reactors and other process units,as well as the possible pathways the trace constituents may take during gasification, are included in the HYGAS Process Description. The HYGAS-based process flow diagram presented in Figure 1,is one example of many possible flow diagrams and includes pollution-abatement and by-product recovery equipment, designed for producing environmentally acceptable substitute natural gas. The tables presented in conjunction with the flow diagram completely characterize the solid, liquid, and gaseous process streams for each of three coals — Illinois No. 6 bituminous coal, Montana subbituminous coal, and lignite. Because the design is based on the concept of minimum liquid-effluent discharge, all process water is recycled to waste-treatment facilities and returned to the process.

A computer program available at IGT to simulate the HYGAS reactor has allowed us to study many permutations of the operating conditions. Because the atmosphere to which the trace elements are subjected determines, to a great extent, the thermodynamically stable forms of each element, the computer program was instrumental in evaluating the effect of process changes, upsets, etc., on the trace element distribution. We found that moderate upsets in temperature and pressure do not significantly alter the values of the operating regions (Appendixes E and F) and, hence, do not change the expected trace element distribution. Although, to be certain, this estimate as well as the effect of larger changes in temperature and pressure on trace element distribution must be verified experimentally.

The extensive free-energy calculations presented in Appendix E were executed concurrently with the analysis of the trace-element content of the coal samples. They represent values of log K_{eq} for reactions likely to occur in the different reaction sections across the operating temperature range, and are based on the most recently determined thermodynamic quantities. The stable forms of the elements studied in each reaction unit are summarized in Appendix E (Table E-3). General trends are for oxides and sulfates to be stable in the pretreater, with sulfides and carbonates being stable in the hydrogasifier. The CO-shift reactor, which is expected to equilibrate the gas mixture, contains sulfides and some elemental forms. Heavier metals — generally the more toxic, volatile species — tend to remain in the neutral, elemental state as gases or fumes. The operating conditions in the pilot plant may tend to favor the sulfide forms for these elements, which would render them more susceptible to complete removal downstream. As neutral species, their volatilities and low solubilities makes them more elusive in the gas-cleaning devices.

IGT's trace constituent analysis of coal, feed, and char samples pretreatment and hydrogasification stages of bench-scale gasification runs served as the basis for the trace-element mass balances found in Tables 4, 6, and 7. Elements showed various levels of loss from pretreater char and from first-and second-stage gasification as summarized in Table 14.

Some elements are retained by the ash material or are lost at low (<10%) levels during gasification of bituminous or lignite coals. These include barium, cobalt, iron, lithium, magnesium, molybdenum, nickel, potassium, samarium, silicon, sodium, and titanium.

A few elements show significant losses during gasification of one coal, but not for the other. For example, when Illinois No. 6 bituminous coal is gasified, calcium, silver, and tin are volatilized by 34%, 64%, and 50%,

Table 14. SUMMARY OF IGT ANALYTICAL RESULTS FOR 38 TRACE AND MINOR ELEMENTS IN FEED AND RESIDUE SAMPLES OF TWO COALS HYDROGASIFIED IN A BENCH-SCALE UNIT

	Illinois No. 6 Bituminous				Montana Lignite		
Element	Feed	Pretreated Residue	Hydrogasified Residue	Loss	Feed	Hydrogasified Residue	Loss
	ppm	ppm	ppm	%	ppm	ppm	%
Sb	1.1	0.78	0.72	35	1.2	0.93	23
As	24	21	16	33	18	8.6	52
Ba	31	30	31	0	1300	1300	0
Be	1.0	0.85	0.76	24	0.98	0.76	22
Bi	1.1	0.94	0.54	51	0.72	0.41	43
B	200	190	180	10	85	61	28
Cd	0.89	0.56	0.21	76	0.72	0.33	54
Ca	3500	2800	2300	34	17,000	17,000	0
Cl	2300	1500	590	74	180	95	47
Cr	15	15	15	0	14	11	21
Co	3.6	3.6	3.6	0	4.4	4.4	0
Cu	19	19	19	0	8.8	6.2	30
F	61	59	45	26	71	45	37
Ge	4.3	4.1	3.9	9	2.7	2.1	22
Fe	14,000	13,500	13,000	7	9200	9300	0
Pb	11	5.8	5.8	47	1.9	1.0	47
Li	33	33	33	0	5.8	5.8	0
Mg	570	600	580	0	5800	5700	2
Mn	48	44	39	19	8.9	8.5	4
Hg	0.12	0.025	0.0045	96	0.73	0.0075	99

Table 14, Cont. SUMMARY OF IGT ANALYTICAL RESULTS FOR 38 TRACE AND MINOR ELEMENTS IN FEED AND RESIDUE SAMPLES OF TWO COALS HYDROGASIFIED IN A BENCH-SCALE UNIT

	Illinois No. 6 Bituminous				Montana Lignite		
Element	Feed	Pretreated Residue	Hydrogasified Residue	Loss	Feed	Hydrogasified Residue	Loss
	ppm			%	ppm		%
Mo	7.0	6.9	6.8	3	2.1	1.9	10
Ni	15	14	14	7	23	21	9
N	10,400	10,400	2400	77	9200	1500	84
K	1700	1700	1700	0	340	330	3
Sm	0.74	0.74	0.74	0	0.51	0.50	2
Se	13	11	7.5	42	1.7	0.58	66
Si	20,000	20,000	20,000	0	13,000	12,000	8
Ag	0.10	0.069	0.036	64	0.24	0.23	4
Na	1400	1500	1500	0	180	170	6
Sr	37	38	37	0	350	230	34
S	38,000	29,400	7800	80	9900	3300	67
Te	8.1	6.3	4.8	41	0.42	0.24	42
Sn	2.0	1.5	1.0	50	1.9	1.8	5
Ti	770	770	750	3	320	340	0
V	17	15	14	18	67	54	19
Yb	0.56	0.55	0.52	7.1	0.36	0.32	11
Zn	49	42	36	27	13	9.5	27
Zr	35	33	35	0	25	22	12

respectively. Roughly one-half of each loss occurs during pretreatment. Losses recorded for calcium, silver, and tin during gasification of nonpretreated, Montana lignite are 0%, 4%, and 5%, respectively. In general, pretreated coals show greater losses of trace elements because another exit pathway is available in the flow scheme. Pretreater chars, tars, oils, and off-gases will contain considerable quantities of trace elements and are part of the sampling program of the test plan.

Elements that undergo considerable volatilization in both coals include arsenic, beryllium, bismuth, cadmium, chlorine, fluorine, lead, mercury, nitrogen, selenium, sulfur, tellurium, vanadium, and zinc. Many of these are, of course, the more toxic elements, toward which environmental concern is directed. Even though the losses of each are high, all are expected to be effectively scrubbed from the product gas stream prior to methanation and recovered in various by-product or waste streams. Tables 4, 6, and 7 are the initial estimates of the fate of trace elements in three examples of HYGAS-based coal gasification complexes.

The sampling and analytical program presented here is the major portion of the test plan. It relies heavily upon the accuracy and precision of the sampling methods, sample preparation, and the analytical techniques used. The parameters connected with each method or technique should be evaluated individually for possible errors. Any inconsistencies must be isolated and improved, if possible. The overall precision and accuracy of the program must be monitored continuously with careful checks.

A comparison between NBS and IGT analytical measurements for four elements in NBS standard reference materials (SRM) is presented in Table 15. IGT values compare closely with NBS values and show good reproducibility. No statistical analysis was attempted on these duplicate determinations. While this type of comparison shows acceptable analytical accuracy and precision, it does not, however, address the difficult problems associated with obtaining dependable samples from a coal gasification plant.

Table 15. ANALYSIS OF NBS STANDARD REFERENCE MATERIALS AT IGT LABORATORIES

Element	Sample Form	NBS Value	IGT Value
		ppm	
Arsenic	Coal	5.9 (±0.6)	5.5, 6.1
	Fly ash	61 (± 6)	59, 57
Lead	Coal	30 (±9)	27, 28
	Fly ash	70 (±4)	69, 67
Manganese	Coal	40 (±3)	39, 38
	Fly ash	493 (±7)	481, 488
Zinc	Coal	37 (±4)	39, 38
	Fly ash	210 (±20)	210, 210

In order to get sufficient data for a statistical treatment, at least 20 samples should be taken at each sampling location during the test program. The precision of a sampling technique for solids may be estimated by comparing the ash content (corrected for SO_3) of one sample with the average ash content of 20 samples. The variation in trace-elements concentration (in the same coal) from one batch to the next is large enough to make them undependable as tracers.

The representativeness of a liquid sample may be tested by measuring the sodium contents of each sample or the quantity of particulate matter in each sample from the same location. There is no true measurement of accuracy in this sampling technique, because of variations in the composition of the feedstock plus minor process upsets even at steady-state conditions. But the problem may be minimized by analysis of large numbers of samples.

The precision of the sample preparation process may be tested by using a reliable analytical method to measure a certain parameter in the sample following the sample-preparation steps. Usually one of the major components in the sample may be measured precisely enough with respect to the reference parameter to estimate the precision of the sample preparation process. The accuracy of the sample preparation process may be estimated along with the analytical methods by using the "known addition" method.

The precision and accuracy of the analytical methods may be tested by repetitively analyzing one sample solution by standard addition. To maintain consistency, this test should also be carried out frequently for NBS and EPA standard reference materials.

The analytical methods presented in Tables 11, 12, and 13 of the "Analytical Methods" section are the most reliable and accurate techniques available for the analysis of trace and minor constituents in solid, liquid, and gaseous samples. Table 11 outlines methods of analysis for 39 minor and trace elements that may be found in solid samples. Alternative techniques are offered for flexibility. Their use depends upon the sample matrix and other possible element interferences. Atomic absorption (AAS) and flame emission spectroscopy (FES) are the major tools for solid sample analysis.

The analytical techniques presented in Table 12 cover the organic and inorganic constituents that may be sequestered in liquid samples. The various oxygen-demand parameters are included here as are the metals, total dissolved and suspended solids, mercaptans, nitrogenous compounds, etc.

Gaseous sample analyses are accomplished largely via flameless AAS and colorimetric methods following a preconcentration step, as summarized in Table 13. The analytical techniques presented are for elements that are likely to appear in any of the gas-sampling streams. The physical properties of less volatile species obviate any need for their analysis.

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APPENDIX A. ANALYSES OF SYNTHANE WATER AND TAR SAMPLES

The liquid effluents from any new commercial gasification facility will necessarily be treated before discharge to ensure protection of the environment. The water introduced into a HYGAS plant will be recycled to water treatment facilities and returned to the process; hence, does not pose a direct pollution problem. Most of the organic material and suspended solids will be removed from the wastewater, perhaps as by-products; however, it is of special interest to consider where each potential pollutant originates in the process.

The analyses that follow in Table A-1 involve the overhead condensate water in Synthane-Process gasification of several different coals.[18] The Synthane Process operates at roughly 1255K (1800 °F) and 40 atmospheres pressure.

Table A-1. WATER AND TAR ANALYSES FROM SYNTHANE[a, b] GASIFICATION , mg/liter (Except pH)

	Synthane Water Condensate		
	Illinois No. 6 Coal	Wyoming Subbit.	N. Dakota Lignite
pH	8.6	8.7	9.2
Suspended Solids	600	140	64
Phenol	2600	6000	6600
COD	15,000	43,000	38,000
Thiocyanate	152	23	22
Cyanide	0.6	0.23	0.1
NH_3	8100	9520	7200
Chloride	500		

	Ultimate Analysis of Tars, Synthane Process	
	Illinois No. 6 Coal	Lignite
Carbon	82.6	83.8
Hydrogen	6.6	7.7
Nitrogen	1.1	1.0
Sulfur	2.8	1.1
C/H	12.5	10.9

[a] Data from Forney *et al*.

[b] No flow rates were reported for the streams where sampling was done.

APPENDIX B. SAMPLE COMPUTER OUTPUT

Three sets of data from computer runs evaluating the effects of different operating conditions on hydrogasifier products are presented in Tables B-1 through B-3. The characteristics used in these calculations are those of Illinois No. 6 seam bituminous coal.

Table B-1 shows data for a case at "standard" conditions, i.e., 8275 kN/m^2 (1200 psia) and 1300 K (1850 °F) in the steam-oxygen gasifier.

The second set of output (Table B-2) is for "runaway" conditions, i.e., high pressure in the reactor (9930 kN/m^2, 1440 psia) and high temperature in the steam-oxygen gasifier (1533K, 2300 °F).

The third set of output (Table B-3) is for a situation of high temperature (1533K, 2300 °F) and low pressure (6620 kN/m^2, 960 psia).

The composition of the gaseous product exiting from the low-temperature reactor (second page of each output set) is used as the basis for calculating the HYGAS operating regions as described in Appendix F. Expressed in lb-mol/hr, the data may be readily converted to mole fractions for comparison with other raw-gas compositions or for use in equilibrium calculations.

A Datacraft 6024 computer was used for these runs. The computer program was written at IGT.

Table B-1, Part 1. CASE 1, STANDARD OPERATING CONDITIONS

```
                                          FEED COAL CHARACTERIZATION
                                          --------------------------

TYPE OF COAL - ILLINOIS NO.6 COAL DATA BASE
------------

TEMPERATURE, DEGREE F      =   600.          FRACTION OF FEED CARHON WHICH IS VOLATILE, LB/LB  =   .1014
FLOW RATE, LB/HR           =    17.2930      FRACTION OF TOTAL VOLATILE CARRON WHICH FORMS
                                                GASEOUS HYDROCARRONS OTHER THAN CH(4)--
COMPOSITION, MASS FRACTION,                            (C(2)H(6) AND C(6)H(6)), LB/LB      =   .1843
                     C  =       .6945        FRACTION OF TOTAL VOLATILE CARRON WHICH FORMS
                     H  =       .0341           CONDENSIBLE OIL AND TAR, LB/LB             =   .2058
                     O  =       .1011        H(2)/C RATIO IN CONDENSIBLE OIL AND TAR, MOLE/MOLE=   .4527
                     N  =       .0127        O/C    RATIO IN CONDENSIBLE OIL AND TAR, MOLE/MOLE=   .0657
                     S  =       .0348        FRACTION OF CARRON IN GASEOUS HYDROCARBONS OTHER
                   ASH  =       .1164           THAN CH(4),AS C(2)H(6) (REMAINDER AS C(6)H(6))
                                                                            MOLE/MOLE  =   .5281
               TOTAL  =      1.0000

KINETIC ACTIVITY FACTOR FOR LOW  RATE REACTION  =  1.0000
KINETIC ACTIVITY FACTOR FOR HIGH RATE REACTION  =   .9390


                                          PROCESS DESCRIPTION
                                          -------------------

RAPID RATE AND DEVOLATILIZATION REACTOR INCLUDED     TEMPERATURE OF LOW  TEMPERATURE REACTOR, DEGREE F     =  1248

RAPID RATE TAKING PLACE IN HTR                       TEMPERATURE OF HIGH TEMPERATURE REACTOR, DEGREE F     =  1720.

ELECTROTHERMAL OR OXYGEN GASIFIER INCLUDED           TEMPERATURE OF ELECTROTHERMAL GASIFIFR, DEGREE F      =  1850.

BALANCE ON RR METHANE                                TEMPERATURE OF FEED STEAM TO ELECTROTHERMAL GASIFIER,
                                                                                          DEGREF F  =   370.
BALANCE ON HTR                                       TEMPERATURE OF FEED STEAM TO HIGH TEMPERATURE REACTOR,
                                                                                          DEGREF F  =  1600.
BALANCE ON OXYGEN GASIFIER                           TEMPERATURE OF LIGHT OIL SLURRY-FEED, DEGREF F         =   148

                                                     TEMPERATURE OF LIGHT OIL VAPORIZER, DEGREE F           =   600.

                                                     SYSTEM PRESSURF, ATM                                   =  81.66
                                                     RAPID RATE METHANF                                     =  .1171
```

Table B-1, Part 2. CASE 1, STANDARD OPERATING CONDITIONS

```
                                       LOW TEMPERATURE REACTOR
                                       -----------------------

SOLIDS FLOW RATE,MOLE/HR   FEED   CHAR PRODUCT   OIL              GAS FLOW RATE,MOLE/HR     FEED                PRODUCT
                                                 PRODUCT
                   C      1.0000       .8986      .0209                      CO            .3215               .3374
                   H(2)    .2925       .0622      .0094                      CO(2)         .3174               .3484
                   O       .1093      0.0000      .0014                      H(2)          .2452               .3644
                   N(2)    .0078       .0050     0.0000                      H(2)O         .3686               .3985
                   S       .0188       .0050     0.0000                      CH(4)         .2430               .2581
                   ASH*   2.0129      2.0129     0.0000                      C(2)H(6)     0.0000               .0049
                                                                             C(6)H(6)     0.0000               .0015
TEMPERATURE, DEGREE F      600.        1250.      1248                       NH(3)        0.0000               .0057
                                                                             H(2)S         .0017               .0155
                                                                             N(2)         0.0000              0.0000

                                                                  TEMPERATURE, DEGREE F     1720.               1248

                                       HIGH TEMPERATURE REACTOR
                                       ------------------------

SOLIDS FLOW RATE,MOLE/HR   FEED     PRODUCT                       GAS FLOW RATE,MOLE/HR     FEED 1    FEED 2    PRODUCT

                   C       .8986       .5454                                 CO            .2399    0.0000      .3215
                   H(2)    .0622       .0377                                 CO(2)         .2328    0.0000      .3174
                   O      0.0000      0.0000                                 H(2)          .3437    0.0000      .2452
                   N(2)    .0050       .0050                                 H(2)O         .6195    0.0000      .3686
                   S       .0050       .0050                                 CH(4)         .0561    0.0000      .2430
                   ASH*   2.0129      2.0129                                 H(2)S         .0017    0.0000      .0017
                                                                             N(2)         0.0000    0.0000     0.0000

TEMPERATURE, DEGREE F     1250.        1720.                      TEMPERATURE, DEGREE F     1850.     1000.     1720.
SOLIDS RESIDENCE TIME = 137.4077 MINUTES.
```

Table B-1, Part 3. CASE 1, STANDARD OPERATING CONDITIONS

```
                                        OXYGEN GASIFIER
                                        ---------------

SOLIDS FLOW RATE,MOLE/HR   FEED      PRODUCT             GAS FLOW RATE,MOLE/HR      FEED 1     FEED 2     PRODUCT

                  C        .5454      .0167                        CO               0.0000     0.0000      .2349
                  H(2)     .0377      .0107                        CO(2)            0.0000     0.0000      .2328
                  O       0.0000     0.0000                        H(2)             0.0000     0.0000      .3437
                  N(2)     .0050      .0050                        H(2)O            0.0000     1.0500      .6195
                  S        .0050      .0033                        CH(4)            0.0000     0.0000      .0561
                  ASH*    2.0129     2.0129                        O(2)              .1374     0.0000     0.0000
                                                                   H(2)S            0.0000     0.0000      .0017
                                                                   N(2)             0.0000     0.0000     0.0000

TEMPERATURE, DEGREE F     1720.       1850.              TEMPERATURE, DEGREE F       370.      1100.      1850.
SOLIDS RESIDENCE TIME =  16.9477 MINUTES.
```

Table B-2, Part 1. HIGH TEMPERATURE, HIGH PRESSURE OPERATING CONDITIONS

```
                               FE-D COAL CHARACTERIZATION
                               --------------------------

TYPE OF COAL - ILLINOIS NO.6 COAL DATA BASE
------------

TEMPERATURE, DEGREE F      =   800.          FRACTION OF FEED CARBON WHICH IS VOLATILE, LB/LB  =   .1014
FLOW RATE, LB/HR           =    17.2930      FRACTION OF TOTAL VOLATILE CARBON WHICH FORMS
                                                GASEOUS HYDROCARBONS OTHER THAN CH(4)--
COMPOSITION, MASS FRACTION,                               (C(2)H(6) AND C(6)H(6)), LB/LB        =   .1843
                     C  =       .6945        FRACTION OF TOTAL VOLATILE CARBON WHICH FORMS
                     H  =       .0341           CONDENSIBLE OIL AND TAR, LB/LB                  =   .2058
                     O  =       .1011        H(2)/C RATIO IN CONDENSIBLE OIL AND TAR, MOLE/MOLE=   .4527
                     N  =       .0127        O/C    RATIO IN CONDENSIBLE OIL AND TAR, MOLE/MOLE=   .0657
                     S  =       .0348        FRACTION OF CARBON IN GASEOUS HYDROCARBONS OTHER
                   ASH  =       .1164           THAN CH(4),AS C(2)H(6) (REMAINDER AS C(6)H(6))
                                                                              MOLE/MOLE  =   .5281
                 TOTAL  =      1.0000

KINETIC ACTIVITY FACTOR FOR LOW  RATE REACTION  =  1.0000
KINETIC ACTIVITY FACTOR FOR HIGH RATE REACTION  =   .9340


                               PROCESS DESCRIPTION
                               -------------------

RAPID RATE AND DEVOLATILIZATION REACTOR INCLUDED      TEMPERATURE OF LOW  TEMPERATURE REACTOR, DEGREE F     =  1592

RAPID RATE TAKING PLACE IN HTR                        TEMPERATURE OF HIGH TEMPERATURE REACTOR, DEGREE F     =  2150.

ELECTROTHERMAL OR OXYGEN GASIFIER INCLUDED            TEMPERATURE OF ELECTROTHERMAL GASIFIER, DEGREE F      =  2300.

BALANCE ON RR METHANE                                 TEMPERATURE OF FEED STEAM TO ELECTROTHERMAL GASIFIER,
                                                                                            DEGREE F  =   370.
BALANCE ON HTR                                        TEMPERATURE OF FEED STEAM TO HIGH TEMPERATURE REACTOR,
                                                                                            DEGREE F  =  1000.
BALANCE ON OXYGEN GASIFIER                            TEMPERATURE OF LIGHT OIL SLURRY-FEED, DEGREE F        =   298

                                                      TEMPERATURE OF LIGHT OIL VAPORIZER, DEGREE F          =   800.

                                                      SYSTEM PRESSURE, ATM                                  =  97.98
                                                      RAPID RATE METHANE                                    =  .1486
```

Table B-2, Part 2. HIGH TEMPERATURE, HIGH PRESSURE OPERATING CONDITIONS

```
                                  LOW TEMPERATURE REACTOR
                                  -----------------------

SOLIDS FLOW RATE,MOLE/HR   FEED    CHAR PRODUCT   OIL            GAS FLOW RATE,MOLE/HR    FEED              PRODUCT
                                                  PRODUCT
                   C      1.0000       .8986      .0209                   CO             .3993               .3635
                   H(2)    .2925       .0622      .0094                   CO(2)          .2858               .3686
                   O       .1093      0.0000      .0014                   H(2)           .2423               .4145
                   N(2)    .0078       .0050     0.0000                   H(2)O          .4656               .4436
                   S       .0188       .0050     0.0000                   CH(4)          .1927               .2072
                   ASH*   2.0129      2.0129     0.0000                   C(2)H(6)      0.0000               .0049
                                                                          C(6)H(6)      0.0000               .0015
TEMPERATURE, DEGREE F      800.       1590.       1592                    NH(3)         0.0000               .0057
                                                                          H(2)S          .0041               .0179
                                                                          N(2)          0.0000              0.0000

                                                                 TEMPERATURE, DEGREE F   2150.               1592


                                  HIGH TEMPERATURE REACTOR
                                  ------------------------

SOLIDS FLOW RATE,MOLE/HR   FEED      PRODUCT                     GAS FLOW RATE,MOLE/HR    FEED 1    FEED 2    PRODUCT

                   C       .8986      .5986                                   CO             .3323    0.0000     .3993
                   H(2)    .0622      .0414                                   CO(2)          .2135    0.0000     .2858
                   O      0.0000     0.0000                                   H(2)           .3316    0.0000     .2423
                   N(2)    .0050      .0050                                   H(2)O          .6772    0.0000     .4656
                   S       .0050      .0050                                   CH(4)          .0319    0.0000     .1927
                   ASH*   2.0129     2.0129                                   H(2)S          .0041    0.0000     .0041
                                                                              N(2)          0.0000    0.0000    0.0000

TEMPERATURE, DEGREE F     1590.      2150.                       TEMPERATURE, DEGREE F   2300.     1000.     2150.
SOLIDS RESIDENCE TIME =    .1917 MINUTES.
```

Table B-2, Part 3. HIGH TEMPERATURE, HIGH PRESSURE OPERATING CONDITIONS

```
                                              OXYGEN GASIFIER
                                              ---------------

SOLIDS FLOW RATE,MOLE/HR   FEED      PRODUCT                    GAS FLOW RATE,MOLE/HR   FEED 1    FEED 2    PRODUCT

                   C       .5984      .0208                               CO            0.0000    0.0000     .3323
                   H(2)    .0414      .0148                               CO(2)         0.0000    0.0000     .2135
                   O      0.0000     0.0000                               H(2)          0.0000    0.0000     .3116
                   N(2)    .0050      .0050                               H(2)O         0.0000    1.0500     .4772
                   S       .0050      .0009                               CH(4)         0.0000    0.0000     .0319
                   ASH*   2.0129     2.0129                               O(2)           .1433    0.0000    0.0000
                                                                          H(2)S         0.0000    0.0000     .0041
                                                                          N(2)          0.0000    0.0000    0.0000

TEMPERATURE, DEGREE F     2150.      2300.                   TEMPERATURE, DEGREE F      370.     1100.     2300.
SOLIDS RESIDENCE TIME =    .3571 MINUTES.
```

Table B-3, Part 1. HIGH TEMPERATURE, LOW PRESSURE OPERATING CONDITIONS

```
                                        FEED COAL CHARACTERIZATION
                                        --------------------------

TYPE OF COAL - ILLINOIS NO.6 COAL DATA BASE
------------

TEMPERATURE, DEGREE F      =   800.          FRACTION OF FEED CARBON WHICH IS VOLATILE, LB/LB  =   .1014
FLOW RATE, LB/HR           =    17.2930      FRACTION OF TOTAL VOLATILE CARBON WHICH FORMS
                                                GASEOUS HYDROCARBONS OTHER THAN CH(4)--
COMPOSITION, MASS FRACTION,                           (C(2)H(6) AND C(6)H(6)), LB/LB      =   .1843
                    C  =      .6945          FRACTION OF TOTAL VOLATILE CARBON WHICH FORMS
                    H  =      .0341             CONDENSIBLE OIL AND TAR, LB/LB              =   .2058
                    O  =      .1011          H(2)/C RATIO IN CONDENSIBLE OIL AND TAR, MOLE/MOLE=   .4527
                    N  =      .0127          O/C    RATIO IN CONDENSIBLE OIL AND TAR, MOLE/MOLE=   .0657
                    S  =      .0348          FRACTION OF CARBON IN GASEOUS HYDROCARBONS OTHER
                  ASH  =      .1164             THAN CH(4),AS C(2)H(6) (REMAINDER AS C(6)H(6))
                                                                              MOLE/MOLE  =   .5281
                TOTAL  =     1.0000

KINETIC ACTIVITY FACTOR FOR LOW  RATE REACTION  =  1.0000
KINETIC ACTIVITY FACTOR FOR HIGH RATE REACTION  =   .9390


                                        PROCESS DESCRIPTION
                                        -------------------

RAPID RATE AND DEVOLATILIZATION REACTOR INCLUDED      TEMPERATURE OF LOW  TEMPERATURE REACTOR, DEGREE F      =  1601

RAPID RATE TAKING PLACE IN HTR                        TEMPERATURE OF HIGH TEMPERATURE REACTOR, DEGREE F      =  2150.

ELECTROTHERMAL OR OXYGEN GASIFIER INCLUDED            TEMPERATURE OF ELECTROTHERMAL GASIFIER, DEGREE F       =  2300.

BALANCE ON RR METHANE                                 TEMPERATURE OF FEED STEAM TO ELECTROTHERMAL GASIFIER,
                                                                                           DEGREE F  =   370.
BALANCE ON HTR                                        TEMPERATURE OF FEED STEAM TO HIGH TEMPERATURE REACTOR,
                                                                                           DEGREE F  =  1000.
BALANCE ON OXYGEN GASIFIER                            TEMPERATURE OF LIGHT OIL SLURRY-FEED, DEGREE F         =   280

                                                      TEMPERATURE OF LIGHT OIL VAPORIZER, DEGREE F           =   800.

                                                      SYSTEM PRESSURE, ATM                                   =  65.32
                                                      RAPID RATE METHANE                                     =  .1138
```

Table B-3, Part 2. HIGH TEMPERATURE, LOW PRESSURE OPERATING CONDITIONS

```
                                                   LOW TEMPERATURE REACTOR
                                                   -----------------------

SOLIDS FLOW RATE,MOLE/HR    FEED    CHAR PRODUCT    OIL                 GAS FLOW RATE,MOLE/HR     FEED              PRODUCT
                                                    PRODUCT
                  C        1.0000       .8986       .0209                          CO               .4597              .4136
                  H(2)      .2925       .0622       .0094                          CO(2)            .2687              .3617
                  O         .1093      0.0000       .0014                          H(2)             .3078              .4899
                  N(2)      .0078       .0050      0.0000                          H(2)O            .4831              .4510
                  S         .0188       .0050      0.0000                          CH(4)            .1502              .1648
                  ASH*     2.0129      2.0129      0.0000                          C(2)H(6)        0.0000              .0049
                                                                                   C(6)H(6)        0.0000              .0015
TEMPERATURE, DEGREE F       800.       1601.       1601                            NH(3)           0.0000              .0057
                                                                                   H(2)S            .0046              .0185
                                                                                   N(2)            0.0000             0.0000

                                                                    TEMPERATURE, DEGREE F          2150.              1601


                                                   HIGH TEMPERATURE REACTOR
                                                   ------------------------

SOLIDS FLOW RATE,MOLE/HR    FEED       PRODUCT                      GAS FLOW RATE,MOLE/HR     FEED 1    FEED 2     PRODUCT

                  C         .8986       .6760                                      CO               .4092    0.0000     .4597
                  H(2)      .0622       .0468                                      CO(2)            .2168    0.0000     .2687
                  O        0.0000      0.0000                                      H(2)             .3786    0.0000     .3078
                  N(2)      .0050       .0050                                      H(2)O            .6374    0.0000     .4831
                  S         .0050       .0050                                      CH(4)            .0300    0.0000     .1502
                  ASH*     2.0129      2.0129                                      H(2)S            .0046    0.0000     .0046
                                                                                   N(2)            0.0000    0.0000    0.0000

TEMPERATURE, DEGREE F      1601.       2150.                        TEMPERATURE, DEGREE F          2300.     1000.     2150.
SOLIDS RESIDENCE TIME =     .1295 MINUTES.
```

Table B-3, Part 3. HIGH TEMPERATURE, LOW PRESSURE OPERATING CONDITIONS

```
                                         OXYGEN GASIFIER
                                         ---------------

SOLIDS FLOW RATE,MOLE/HR   FEED      PRODUCT                  GAS FLOW RATE,MOLE/HR    FEED 1    FEED 2    PRODUCT

                   C       .6760      .0200                                CO          0.0000    0.0000     .4092
                   H(2)    .0468      .0163                                CO(2)       0.0000    0.0000     .2168
                   O      0.0000     0.0000                                H(2)        0.0000    0.0000     .3784
                   N(2)    .0050      .0050                                H(2)O       0.0000    1.0500     .6376
                   S       .0050      .0003                                CH(4)       0.0000    0.0000     .0300
                   ASH*   2.0129     2.0129                                O(2)         .2151    0.0000    0.0000
                                                                           H(2)S       0.0000    0.0000     .0046
                                                                           N(2)        0.0000    0.0000    0.0000

TEMPERATURE, DEGREE F     2150.      2300.                    TEMPERATURE, DEGREE F     370.     1100.     2300.
SOLIDS RESIDENCE TIME =    .3974 MINUTES.
```

APPENDIX C. FLOW RATE DETERMINATION – SCALING FACTORS

The flow rates from Tables 1, 2, and 3 of the text were taken directly from examples of IGT process designs for commercial-scale coal gasification plants based on bituminous, subbituminous, and lignite coals. The English units have been converted to the corresponding SI-approved metric notation. Variations in each process are footnoted at the end of each table. The design for a lignite-coal-based plant incorporated the use of a magnetohydrodynamic (MHD) unit to produce process power. The MHD unit did effect the quantities of off-site coal required in the process, as compared to coal-fired steam boilers.

Sample feeds, intermediate products, and residues from the bench-scale gasification of Illinois No. 6 seam bituminous and Montana lignite coals were analyzed for trace elements at IGT. No trace analysis has been completed on a subbituminous coal. The analyses were reported in parts per million of trace element per unit weight of dry coal fed to the bench-scale reactor. The flow rates of the three coals fed to a commercial-size reactor were calculated as –

	kg/s (dry)
Illinois No. 6 Bituminous	133.29
Montana Subbituminous	148.36
Lignite	177.04

These flow rates do not include steam-plant feed or pretreater losses. The data from the trace analyses and the flow rates were used to calculate the corresponding trace-element flow rates in a commercial plant.

The calculations for Table 4 (Illinois No. 6 coal) were straightforward, requiring only scaling by a common factor.

The lignite design calls for about 19% more dry coal fed to the hydrogasifier than the subbituminous design, and 1.193239 was used as the factor to calculate the flow rates for trace elements shown in Table 6 for subbituminous coal. To simplify the preparation of this table it was assumed that subbituminous coal has approximately the same trace-element composition as lignite coal. (The uncertainty of this assumption was addressed earlier in the report section on Process Steps, page 30).

Thus, based on dry coal feed, the flow rates of each trace element in Table 7 are a factor of 1.193239 greater than the corresponding flow rate shown in Table 6.

Scaling Factor

To determine the corresponding values of trace-element flow rates expected from a commercial plant based on data from the HYGAS pilot plant, the following factors should be used:

HYGAS Capacity	0.787 kg/s raw coal (75 tons/day)
Moisture Content of Feed Coals, %	
Bituminous	6.5
Subbituminous	22
Lignite	35

Flow Rates of Dry Coal Required, kg/s	Hydrogasifier
Bituminous	133.29
Subbituminous	148.36
Lignite	177.04

Conversion Factors Based on Dry Coal	Hydrogasifer
Bituminous	181
Subbituminous	241.5
Lignite	345.9

Note that the lignite factor is 1.9 times the bituminous factor for the hydrogasifier feed and 1.4 times the corresponding subbituminous factor.

Energy Flow Rates

The summary table presented in the HYGAS Process Description section is reproduced here as related information. The moisture content, heating values (HHV), and process mass and energy flow rates for three coals are shown below with some additional data. Note that the quantities of coal energy to the "Process" and to the "Offsites" are quite similar for the bituminous and subbituminous coals, differing from each other by less than 1 and 5 percent, respectively.

Coal	Moisture Content, %	Heating Value, Dry Basis	Raw Coal to Plant	Coal to Process	Coal to Offsites	Product SNG Energy	Process Efficiency
		MJ/kg (Btu/lb)	GJ/s (kg/s)				%
Lignite[a]	35	26.2839 (11,300)	4.9902 (292.09)	4.6532 (272.36)	0.3370 (19.72)	3.0528	71.7
Subbituminous	22	26.2865 (11,301)	5.0750 (248.61)	3.8828[b] (158.68)	1.1922[b] (48.72)	3.0528	67.2
Bituminous	6.5	29.3142 (12,603)	5.0513[c] (183.29)	3.9151[c] (133.29)	1.1362[c] (38.68)	3.0528	66.2

[a] A magnetohydrodynamic (MHD) unit provided energy for an electrothermal gasifier in this design.

[b] Partially dried coal contains 6.5% moisture.

[c] Dried coal contains <1% moisture.

The overall energy efficiency for the subbituminous design is 67.2 percent; that for the bituminous design is 66.2 percent. Because of the use of a magnetohydrodynamic unit for electric power generation in the lignite design, the energy requirements are not comparable to the other two designs. However, the efficiency of this early lignite-based design was calculated at 71.7 percent.

APPENDIX D. DISCUSSION OF PROCESS UNITS AND REACTIONS

To determine the thermodynamically stable form of each trace (or minor) element in coal in the HYGAS operation, attention was given to the temperatures of each reaction unit, and to pressure when the reaction was affected by the pressure. Otherwise, the stable form was calculated on a thermodynamic basis, and other physical properties indicated the phase of the material. For volatile elements and compounds, the vapor pressures were calculated at the temperatures considered.

For purposes of this study, the primary reaction units are the pretreater, the high-temperature and steam oxygen gasifiers, and the CO-shift reactor. The operating conditions and typical gas composition for each unit are developed in the following paragraphs.

Pretreater (for Agglomerating Coals): 700K (800°F), 115 kN/m^2 (2 psig)

In the pretreater, the atmosphere to which the coal, including its mineral matter, is exposed differs throughout the bed and even in different zones of a particle. Air enters at the bottom of the fluidized bed, while the gaseous matter devolatilized from the coal contains hydrogen, hydrocarbons, water, and oxides of carbon and sulfur. Carbon monoxide and carbon dioxide are also formed during partial combustion of the coal particles. The pretreater off-gas contains all of these products as well as unreacted oxygen.

The reaction of oxygen with the particles occurs only in a peripheral zone of the particles, while partial devolatilization occurs throughout. Because of the mixing in the fluidized bed, the residence time, and thus the extent of the reactions (that of the mineral matter as well as oxidation and devolatilization of the coal substance), may vary greatly from particle to particle.

An approximate analysis of pretreater off-gases for Illinois No. 6 coal is —

	mole%		mole%
CO	3.49	C_3H_8	0.46
CO_2	6.26	N_2	65.09
H_2O	20.11	O_2	2.37
CH_4	0.46	Ar	0.84
C_2H_6	0.23	SO_2	0.69

This gas stream also contains the volatilized trace elements listed in Table 4, under Pretreater Losses.

High-Temperature Reactor and Steam-Oxygen Gasifier: 1300K (1880 °F), 6995 to 8375 kN/m² (1000 to 1200 psig)

The conditions of the HTR and the steam-oxygen gasifier (OG) are the most extreme of the gasification facility. At 1300K, many trace elements are in the vapor phase and available for reaction with other process gases. The reactors operate as fluidized-bed reactors, and the atmosphere to which trace and minor elements are exposed is highly reducing. The typical gaseous components exiting from the light-oil vaporizer for a bituminous, subbituminous, and lignite coal are listed below:

Component	Bituminous	Subbituminous	Lignite
		Mole %	
CO	19.84	21.97	11.49
CO_2	14.83	14.11	14.85
H_2	20.66	21.18	14.51
H_2O	16.66	17.81	29.39
CH_4	13.04	9.76	16.67
C_2H_6	0.13	0.79	0.81
C_6H_6	0.43	0.18	0.13
NH_3	0.54	0.15	--
HCN (C_3H_8)	0.03	0.01	(0.27)
H_2S	1.16	0.19	0.24
Oil	12.62	13.83	11.28
COS	0.01	0.00186	--
N_2	0.05	0.01	0.36
	100.00	100.00	100.00

Water-Gas Shift Reactor: 560K (550 °F), 6995 to 8375 kN/m² (1000 to 1200 psig)

The carbon monoxide-shift (CO-shift) reactor is a fixed-bed reactor using a cobalt-molybdenum catalyst in which the gaseous compounds reach equilibrium. The catalyst is tolerant of sulfur compounds and oils in the feedstock, and it can withstand the high system pressure and inadvertent upsets that could introduce water onto the hot catalyst. Typical CO-shift reactor feed compositions are listed below for the three types of coals:

Component	Bituminous	Subbituminous	Lignite
	Mole %		
CO	16.74	19.31	8.53
CO_2	12.51	12.40	9.78
H_2	17.42	18.62	29.81
H_2O	38.84	38.39	24.91
CH_4	11.00	8.58	24.58
C_2H_6	0.36	0.69	1.20
C_6H_6	0.11	0.15	0.26
NH_3	0.45	0.13	--
HCN (C_3H_8)	0.03	0.01	(0.40)
H_2S	0.98	0.16	--
Oil	1.51	1.55	--
COS	0.01	--	--
N_2	0.04	0.01	0.53
	100.00	100.00	100.00

Reactions

The reactions studied were those considered likely to occur with the more reactive gaseous components, i.e., oxygen and carbon dioxide in the pretreater (but not nitrogen or water), and hydrogen, hydrogen sulfide, carbon dioxide, carbon monoxide, and water in the hydrogasifier. A computer program was used to calculate the free energy changes (ΔG) for each reaction as a function of temperature. Then the equilibrium constants were calculated from the equation —

$$\Delta G = -RT \ln K_{eq}$$

where ΔG is the free energy change (cal/g-mol), R is the gas constant (cal/g-mol-K), and T is the absolute temperature (K). The equilibrium constant (K_{eq}) is described in Appendix F in connection with the determination of operating regions. The results of all these calculations are tabulated in Table E-2, Appendix E. Plots of log K_{eq} versus temperature for several kinds of reactions are included later in this report. (See Figures E-3 through E-21, Appendix E.)

The earlier equilibrium calculations included oxidation reactions for carbides and nitrides; however, a literature investigation of naturally occurring nitrides and carbides failed to reveal any (except carbides in some iron meteorites). Later calculations concentrated on the typical modes of trace and minor elements in coal as reported in the literature. (See Bibliography entries 6, 7, 20, 34, 45, and 50.) Table 5 (refer to main text) summarizes the literature information as to the possible modes of occurrence of trace elements in coals. Thus, for example, cadmium exists in coals as cadmium sulfide (CdS), and calculations were made with CdS as a reactant.

The reactions for the three reaction areas are listed below:

Pretreater	$MS + 3/2\ O_2$	$\rightleftarrows$	MSO_3[*]
	$MS + 2O_2$	$\rightleftarrows$	MSO_4
	$MS + 3/2\ O_2$	$\rightleftarrows$	$MO + SO_2$
	$MO + CO_2$	$\rightleftarrows$	MCO_3
	MSO_4	$\rightleftarrows$	$MO_2 + SO_2$
HTR, OG, CO-Shift	$MS + H_2$	$\rightleftarrows$	$M(s,g) + H_2S$
	$MO + H_2$	$\rightleftarrows$	$M(s,g) + H_2O$
	$MS + H_2O$	$\rightleftarrows$	$MO + H_2S$
	$MS + CO_2 + H_2O$	$\rightleftarrows$	$MCO_3 + H_2S$
	$MSO_4 + H_2$	$\rightleftarrows$	$MSO_3 + H_2O$
	$MSO_3 + 3H_2$	$\rightleftarrows$	$MS + 3H_2O$
	$MO + CO_2$	$\rightleftarrows$	MCO_3
	$MO + 2HCl$	$\rightleftarrows$	$MCl_2 + H_2O$
	$MS + 2HCl$	$\rightleftarrows$	$MCl_2 + H_2S$
	$MO + 2HF$	$\rightleftarrows$	$MF_2 + H_2O$

---

[*] M refers to the elements in this study

Some other reactions were investigated thermodynamically where data were available. These involved nitride or carbide hydrolysis, hydrogenation or oxidation, and hydride formation:

$$MS + 2H_2 \rightleftharpoons MH_2 + H_2S$$
$$MO + 2H_2 \rightleftharpoons MH_2 + H_2O$$
$$M_2C_3 + 2H_2S + 4H_2 \rightleftharpoons 2MS + 3CH_4$$
$$MC_2 + H_2S + 3H_2 \rightleftharpoons MS + 2CH_4$$
$$M_2C + CO_2 + 2COS \rightleftharpoons 2MS + 4CO$$
$$M_2C + 2H_2S \rightleftharpoons 2MS + CH_4$$
$$M_3N_2 + 3H_2O \rightleftharpoons 3MO + 2NH_3$$
$$M_3N_2 + 6H_2 \rightleftharpoons 3MH_2 + 2NH_3$$

Calculations were done to compare the relative stabilities of chloride compounds with first- and second-period oxides and with $BeCl_2$ or $MgCl_2$, such as —

$M_2O + BeCl_2 \rightleftharpoons 2MCl + BeO$ (See Figure E-16.)

$M_2O + MgCl_2 \rightleftharpoons 2MCl + MgO$ (See Figure E-17.)

Finally, the formation of $BeH_2(g)$ and the reactions of $KO(g)$ were investigated:

$$BeS + 2H_2 \rightleftharpoons BeH_2(g) + H_2S$$
$$BeO + 2H_2 \rightleftharpoons BeH_2(g) + H_2O$$
$$Be_2C + 4H_2 \rightleftharpoons 2BeH_2(g) + CH_4$$
$$2KO(g) + H_2S \rightleftharpoons K_2S(s) + H_2O + 1/2O_2$$
$$2KO(g) + H_2S \rightleftharpoons K_2S(s) + H_2O_2$$
$$KO(g) + 3/2H_2 \rightleftharpoons KH(g) + H_2O$$

As this work progressed, gaps in the data interfered with the complete and detailed analysis that was our aim. It is apparent that even though interest is growing in trace-element research, considerable work is required in the area of thermodynamics.

Where data were not available, not applicable to a certain temperature range, or of uncertain or questionable validity, the similarity in physical and thermodynamic properties of compounds formed from elements in the same period of the Periodic Table was used as a basis on which to interpolate potential results. Some generalizations can be made concerning the trace elements on this basis. For example, the first period elements tend to favor carbonate formation in the hydrogasifier. The stable forms of the elements in the Periodic Table range from carbonates on the left, to oxides, to sulfides, and to non-metallic hydrides on the right. Many heavy metals tend to remain in the elemental form. Of course, some elements are exceptions to this generalization. As far as the data indicate, sodium chloride, zircon, boron fluoride, and tin (II) chloride are stable in the hydrogasifier.

For all thermodynamic calculations in the three main reaction units, the operating region was determined and compared with the equilibrium constant. If the value of the operating region was less than the calculated value of K_{eq}, the reaction proceeded as written. If the value was greater, the reverse reaction was assumed to occur. This assumption follows directly from thermodynamic considerations and allows for sufficient time to equilibrate. For example, in the case of the reaction

$$PbS(s) + H_2O(g) \rightleftarrows PbO(s) + H_2S(g)$$

occurring in the steam-oxygen gasifier at 1300K, the value of log K_{eq} is −4.417. The value of the operating region (determined from Table E-1, Appendix E, for the reaction type – $MS + H_2O \rightleftarrows MO + H_2S$) is −1.16. The value of log K_{eq} is less than the value of the operating region, therefore, the reverse reaction is favored. (See Appendix E for additional examples.) This study does not take into account the kinetics and reaction rates of the individual components, the complex problems associated with heterogenous reactions, or the effects of diffusion. Thus, it may be possible for an oxide to exist in the gasifier when thermodynamically it should be a sulfide.

Similarly, a sulfide may not be completely oxidized in the pretreater, but may exit as a sulfite or sulfide. Gaseous reactions that are expected to occur in the CO-shift reactor will be catalyzed readily.

When predicting the fate of trace elements, the problems are multiple, as the actual form of an element may be quite different from the calculated form.

With continued research and the analysis of HYGAS process and by-product streams, these questions will be more readily answered, contributing to the understanding of possible trace-element emissions and to the design of more environmentally sound process.

APPENDIX E. Presentation and Discussion of Thermodynamic Calculations: Tables and Graphs

The following tables and graphs are the result of computer and other calculations made to determine the equilibrium constants (K_{eq}) for many of the reactions more likely to occur in a coal-gasification plant.

The tables list the elements, each followed by the relevant reactions (oxidation) of the pretreater, and the reduction reactions (hydrolysis, hydrogenation, carbonation, or exchange) of the hydrogasifier and CO-shift reactor. Miscellaneous reactions are presented when the physical properties of an element warrant — such as low bubble point, high vapor pressure, or toxicity. Across from each reaction, the log of the equilibrium constants (log K_{eq}) is listed for temperatures encountered in the major reaction units: 1300, 700, and 600K. Values for other temperatures are presented when the available data did not extend to 1300K. Occasionally, data were estimated through extrapolation.

Equilibrium curves for pretreater, hydrogasifier, and CO-shift reactions are presented in Figures E-1 to E-19. The ordinate is log K_{eq}; the abscissa is temperature in degrees Kelvin (K). The first- and second-period elements — lithium, sodium, potassium, beryllium, magnesium, calcium, strontium, and barium — are analyzed in detail in these graphs. The periodic nature of their thermodynamic properties is evident and can be used to extend data to other, less documented elements with confidence.

Figures E-1, E-2, and E-3 indicate that the oxidized form of these elements is favored thermodynamically in the pretreater. Figure E-4 shows that only beryllium chloride and magnesium chloride would tend to oxidize in the pretreater. The other reactions are possible, though unlikely, provided that fluorine and chlorine gas partial pressures are small enough to draw the equilibrium to the right.

Carbonate-forming reactions are presented in Figures E-5 through E-8. For the first period oxides or sulfides, carbonates are the stable form. The heavier second-period oxides and sulfides will form carbonates preferentially in the CO-shift reactor (but not beryllium oxide), while the operating conditions in the hydrogasifier favor carbonate formation from barium oxide, strontium oxide, beryllium sulfide, magnesium sulfide, strontium sulfide, and barium sulfide. In cases where the operating region overlaps the plotted equilibrium curve, such as in Figures E-7 and E-8, the direction of the reaction may be evaluated by Le Chatelier's Principle. This principle states that:

> "Any change in one of the variables that determines the state of a system in equilibrium causes a shift in the position of equilibrium in a direction which tends to counteract the change in the variable under consideration."

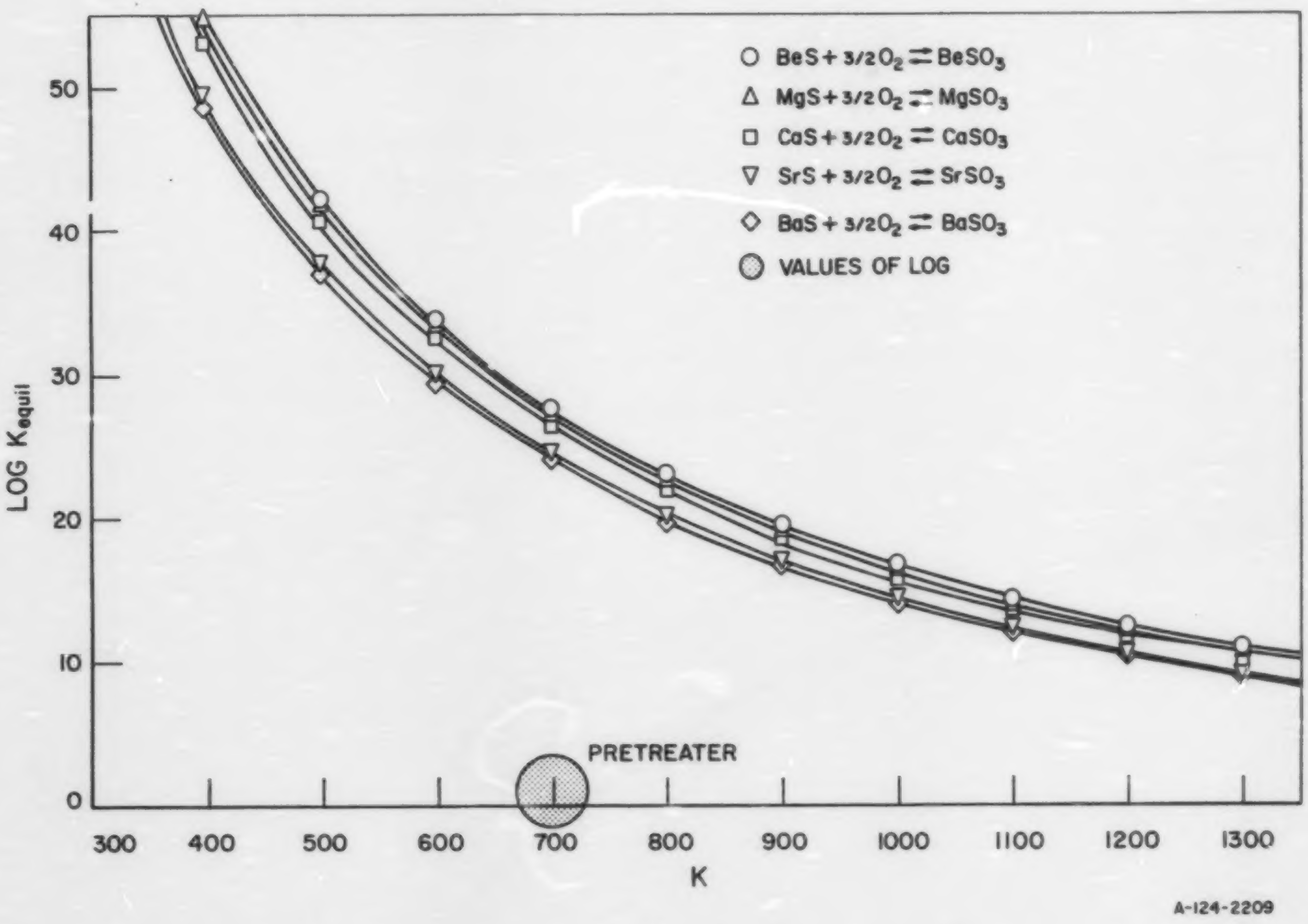

Figure E-1. OXIDATION REACTIONS OF SECOND-PERIOD SULFIDES TO SULFITES

Values of Log $\left[1/(P_{O_2})^{3/2}\right]$ at 600 K = * (CO-Shift)
700 K = 1.02 (Pretreater)
1300 K = * (HYGAS)

*The partial pressure of oxygen in these units is vanishingly small. The value of log approaches ∞.

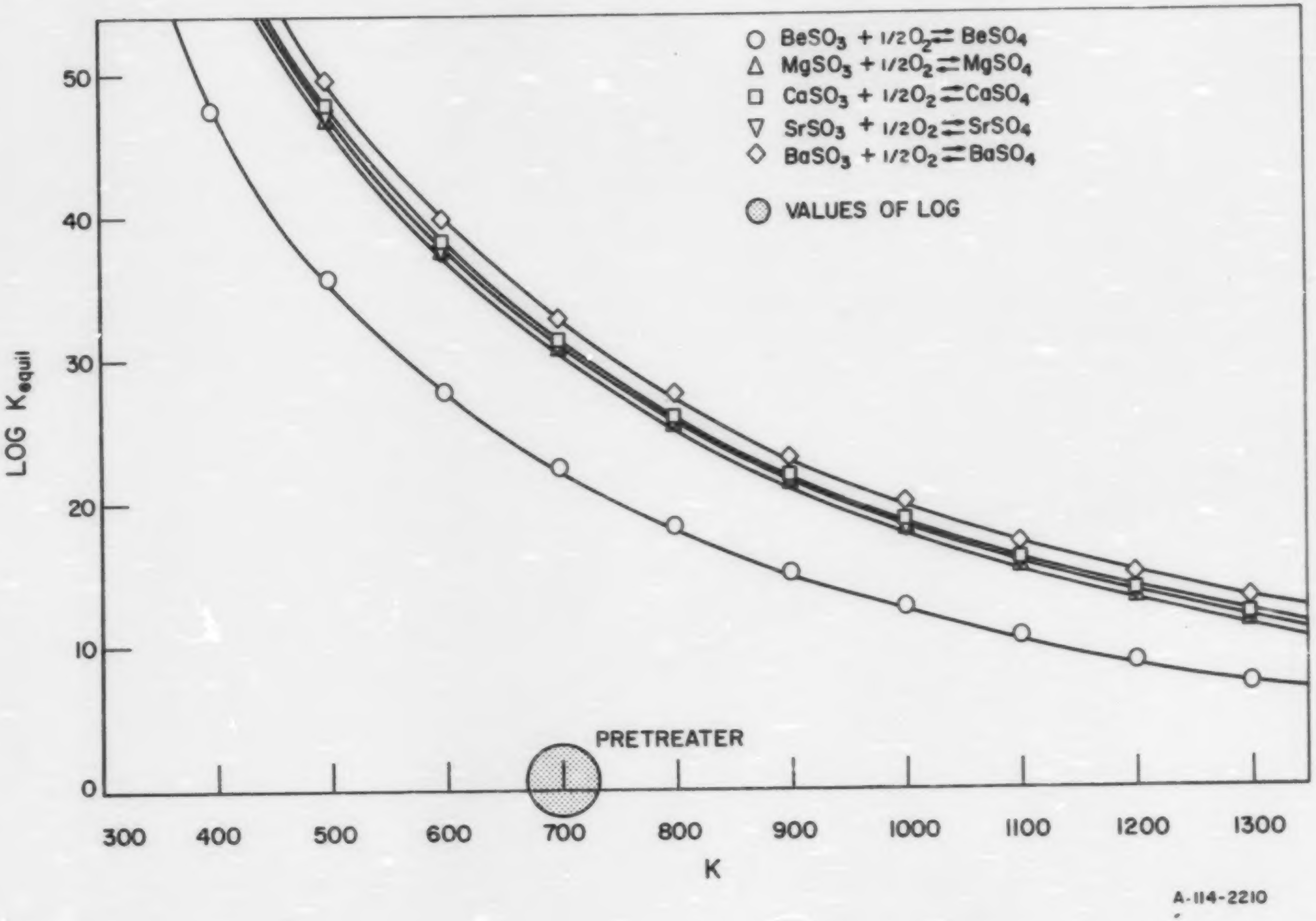

Figure E-2. OXIDATION REACTIONS OF SECOND-PERIOD SULFITES TO SULFATES

Values of Log $\left[1/(P_{O_2})^{1/2}\right]$ at 600 K = * (CO-Shift)
700 K = 0.34 (Pretreater)
1300 K = * (HYGAS)

*The partial pressure of oxygen in these units is vanishingly small. The value of log approaches ∞.

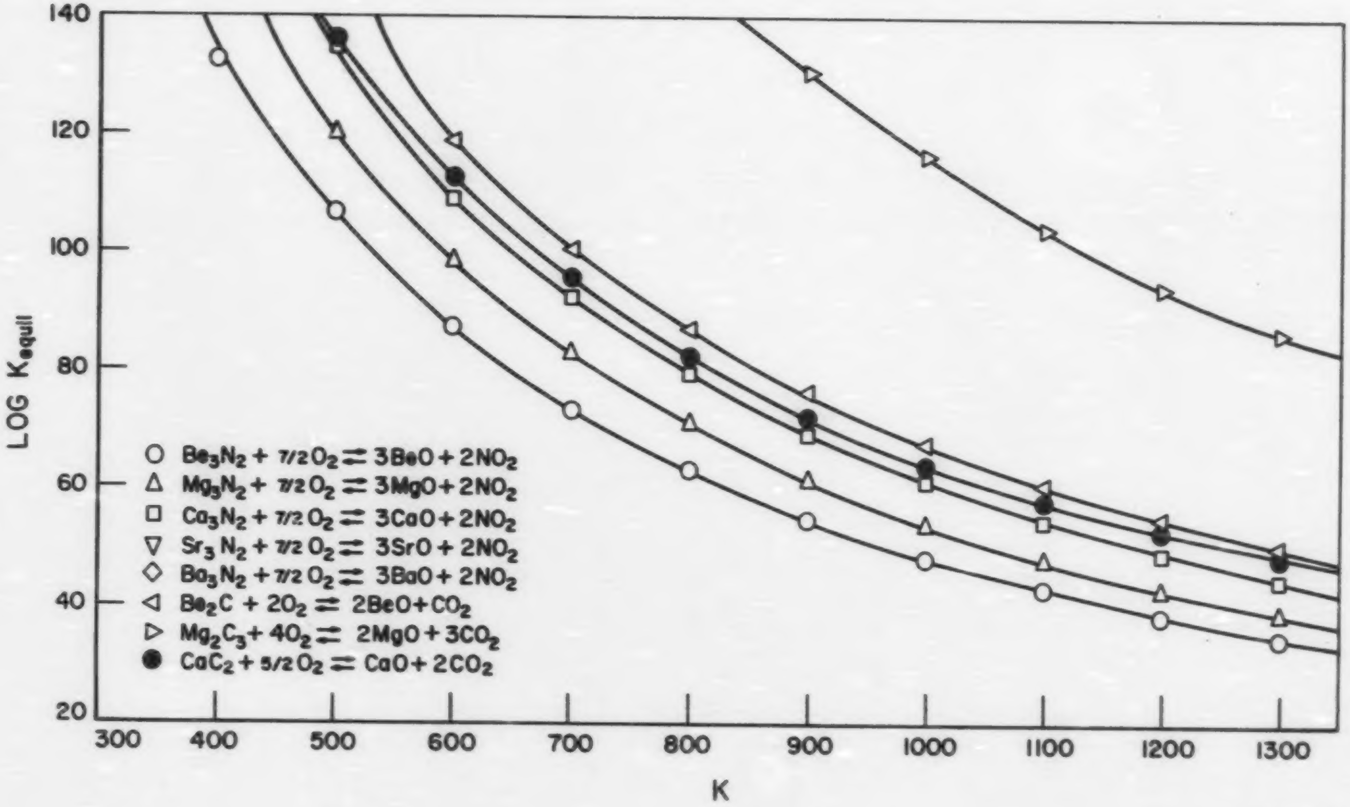

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Figure E-3. OXIDATION REACTIONS OF SECOND-PERIOD NITRIDES AND CARBIDES TO OXIDES

Assuming 10 ppm NO_2 in the NO_2-Forming Reactions, at 700 K, the

Values of $\text{Log}\,[(P_{NO_2})^2/(P_{O_2})^{7/2}] = -7.63$ (Pretreater)

◁ $\text{Log}\,[(P_{CO_2})/(P_{O_2})^2] = 0.15$ (Pretreater)

▷ $\text{Log}\,[(P_{CO_2})^3/(P_{O_2})^4] = -0.90$ (Pretreater)

○ $\text{Log}\,[(P_{CO_2})^2/(P_{O_2})^{5/2}] = -0.71$ (Pretreater)

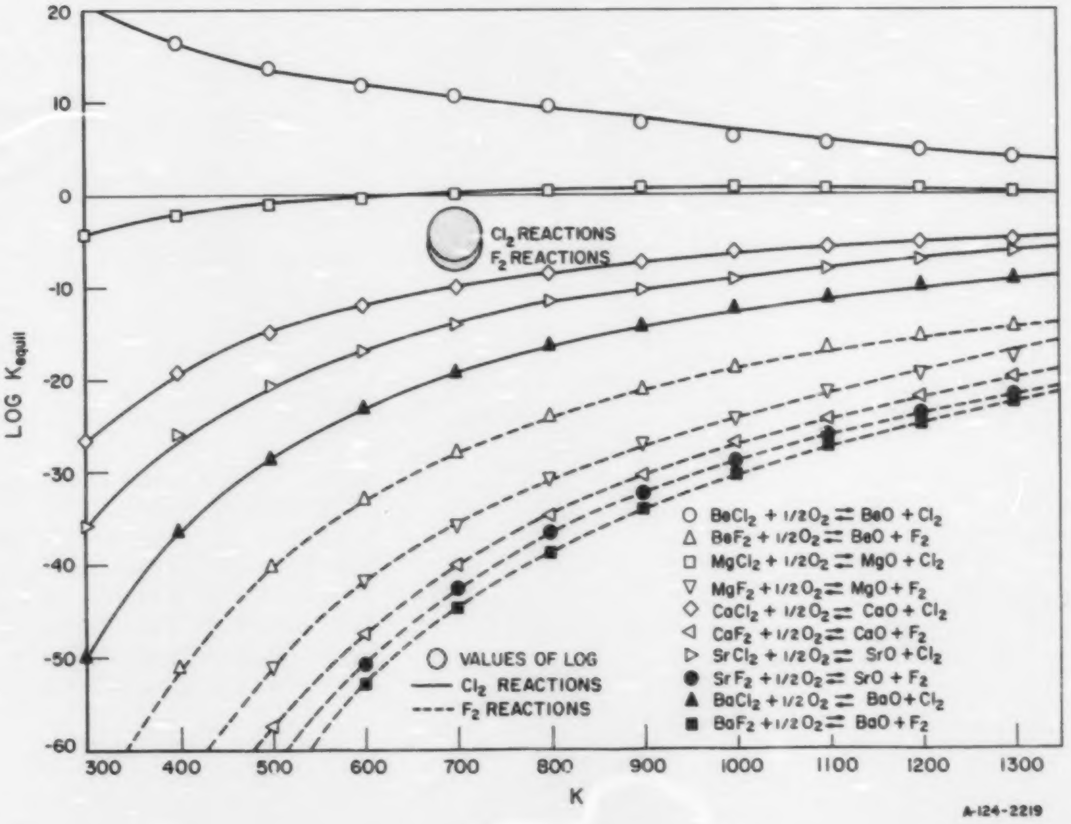

Figure E-4. OXIDATION REACTIONS OF SECOND-PERIOD CHLORIDES AND FLUORIDES TO OXIDES

Assuming Cl_2 = 10 ppm and F_2 = 1 ppm in the Pretreater, at 700 K, the

Values of $\text{Log}\left[(P_{Cl_2})/(P_{O_2})^{1/2}\right] = -4.66$

$\text{Log}\left[(P_{F_2})/(P_{O_2})^{1/2}\right] = -5.66$

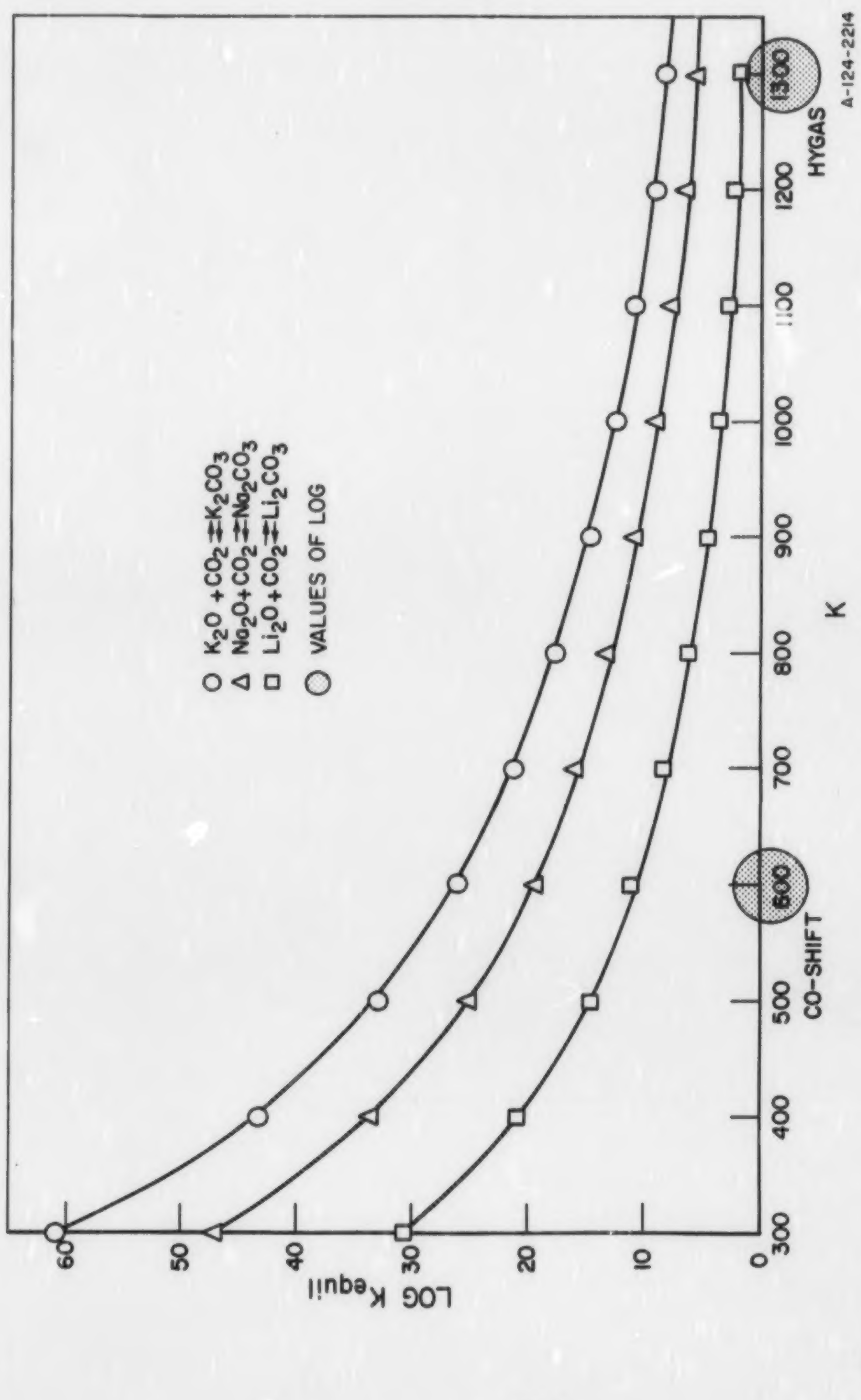

Figure E-5. CARBONATE-FORMING REACTIONS OF FIRST-PERIOD OXIDES

Values of Log $(1/P_{CO_2})$ at 600 K = −1.36 (CO-Shift)

1300 K = −1.17 (HYGAS)

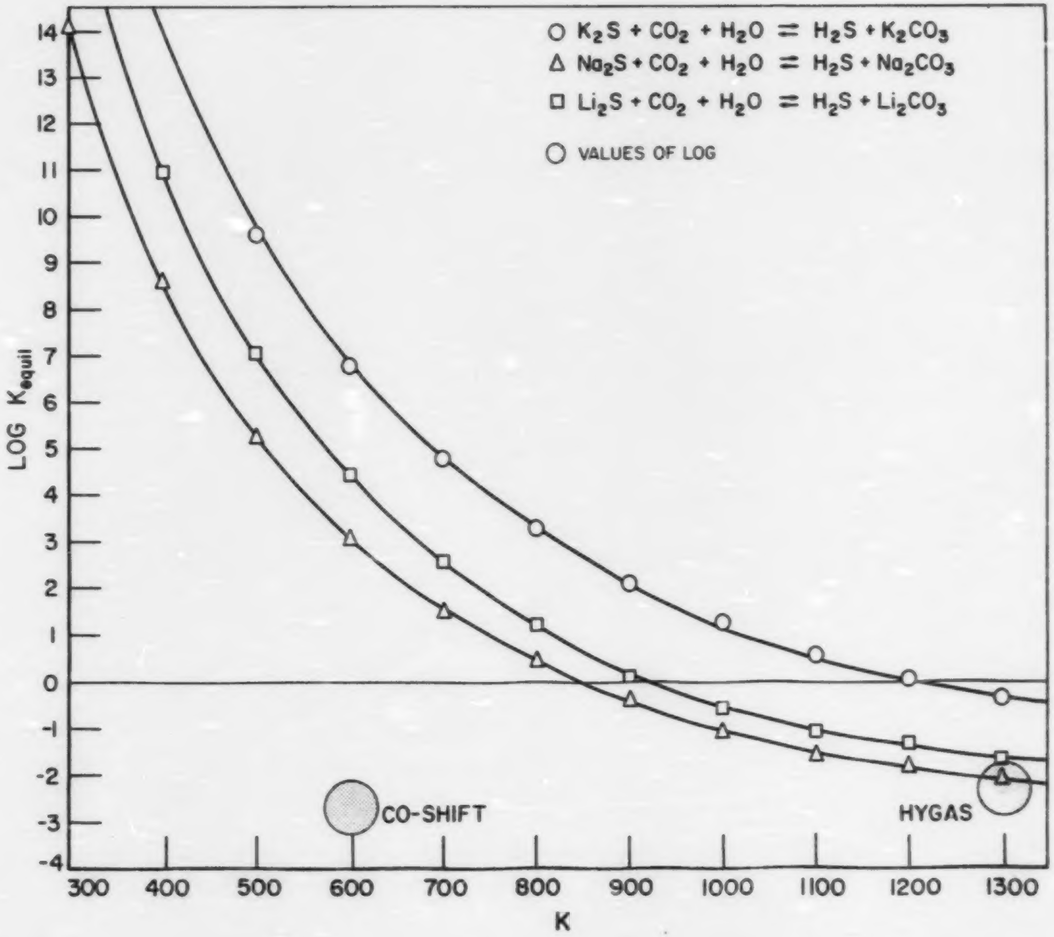

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Figure E-6. CARBONATE-FORMING REACTIONS OF FIRST-PERIOD SULFIDES

Values of Log $\left[(P_{H_2S})/(P_{H_2O})(P_{CO_2})\right]$ at 600 K = −2. 71 (CO-Shift)
1300 K = −2. 33 (HYGAS)

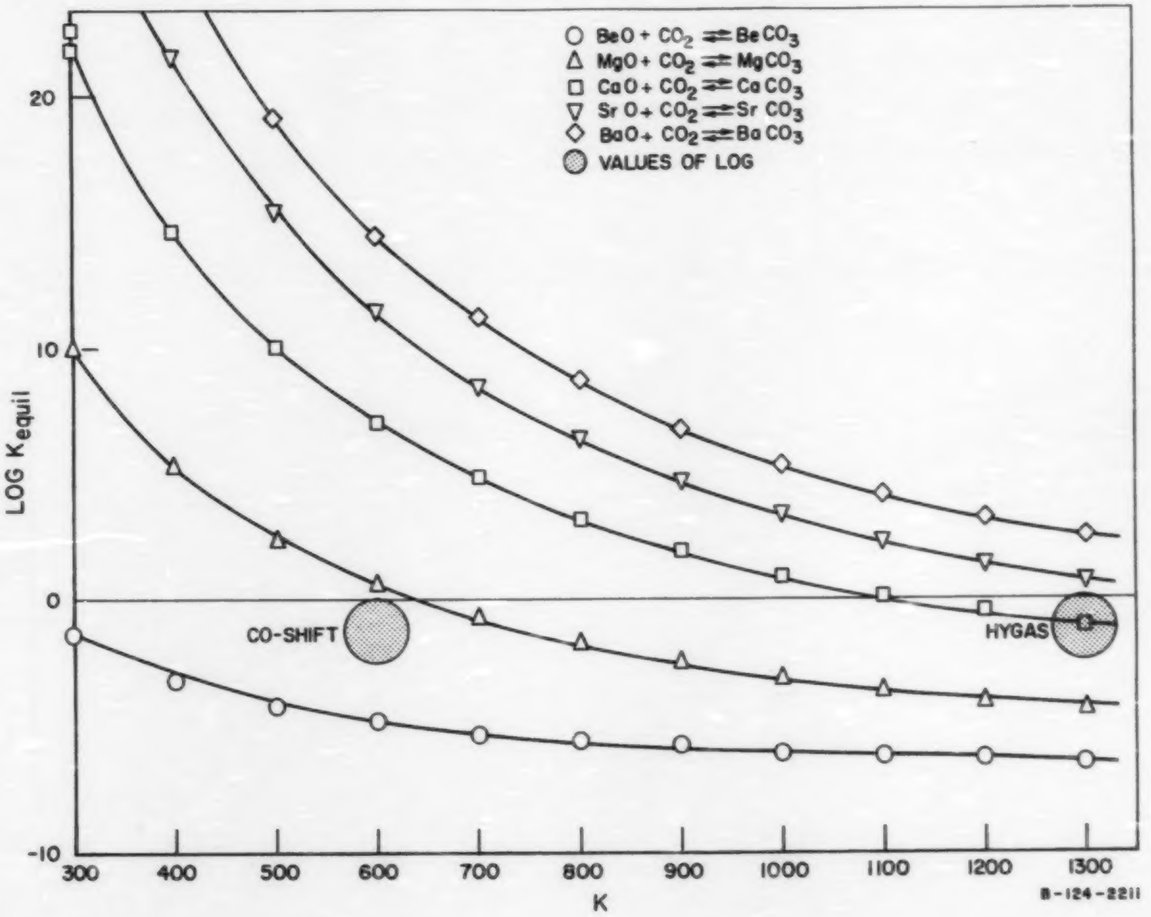

Figure E-7. CARBONATE-FORMING REACTIONS OF SECOND-PERIOD OXIDES

Values of Log $(1/P_{CO_2})$ at 600 K = −1.36 (CO-Shift)
1300 K = −1.17 (HYGAS)

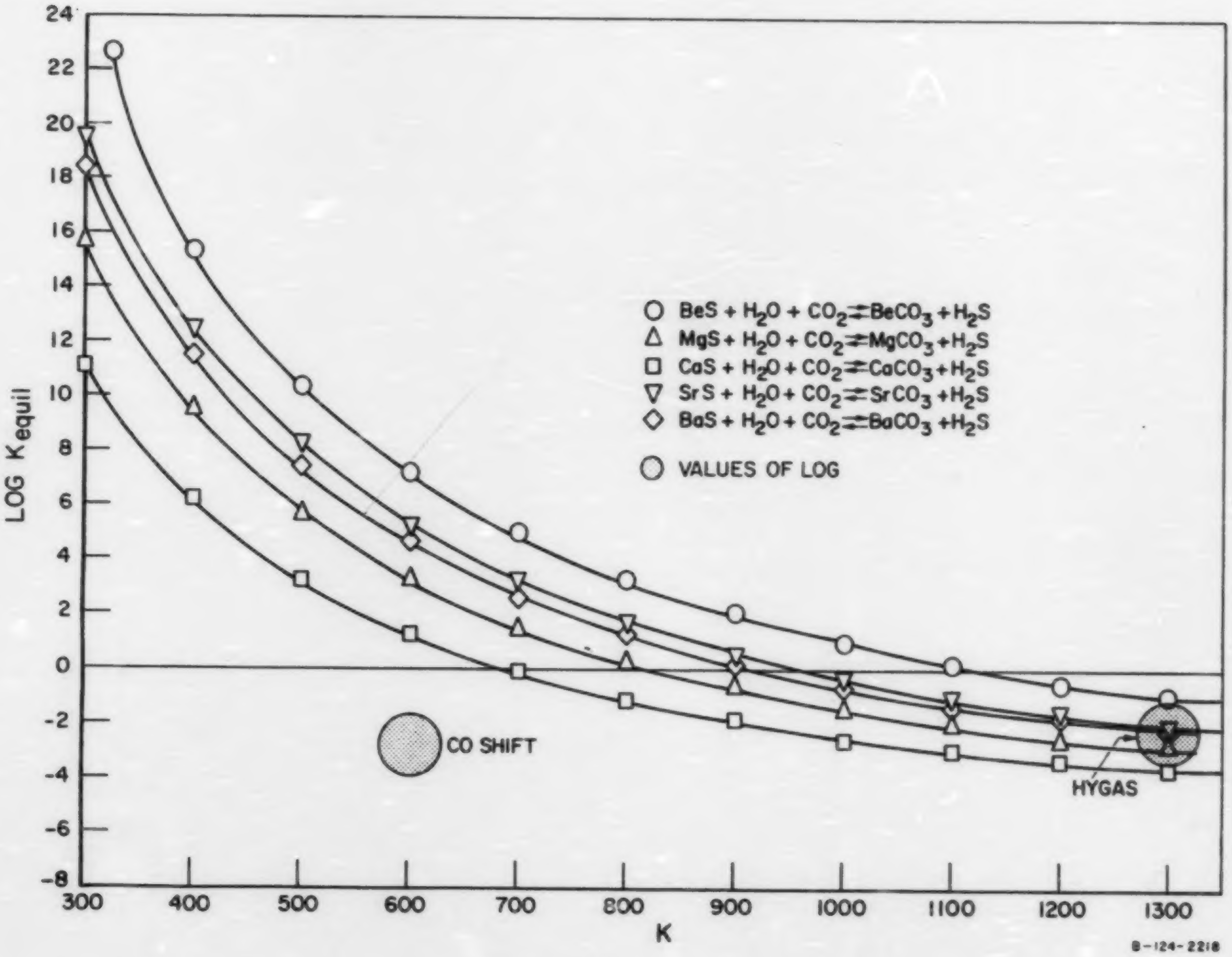

Figure E-8. CARBONATE-FORMING REACTIONS OF SECOND-PERIOD SULFIDES

Values of Log$[(P_{H_2S})/(P_{H_2O})(P_{CO_2})]$ at 600 K = –2.71 (CO-Shift)
1300 K = –2.33 (HYGAS)

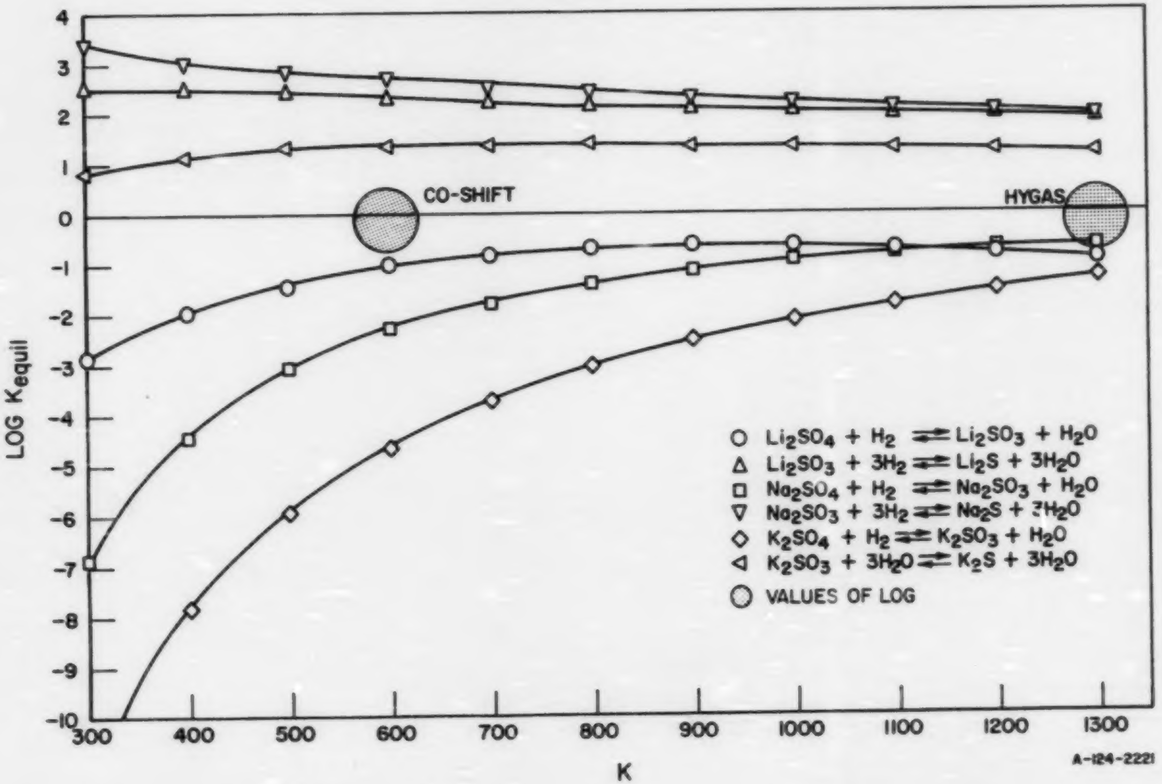

Figure E-9. REDUCTION REACTIONS OF FIRST-PERIOD SULFATES TO SULFITES TO SULFIDES

Values of $\mathrm{Log}\left[(P_{H_2O})/(P_{H_2})\right]$ at 600 K = –0.07 (CO-Shift)

1300 K = –0.09 (HYGAS)

$\mathrm{Log}\left[(P_{H_2O})^3/(P_{H_2})^3\right]$ at 600 K = –0.22 (CO-Shift)

1300 K = –0.28 (HYGAS)

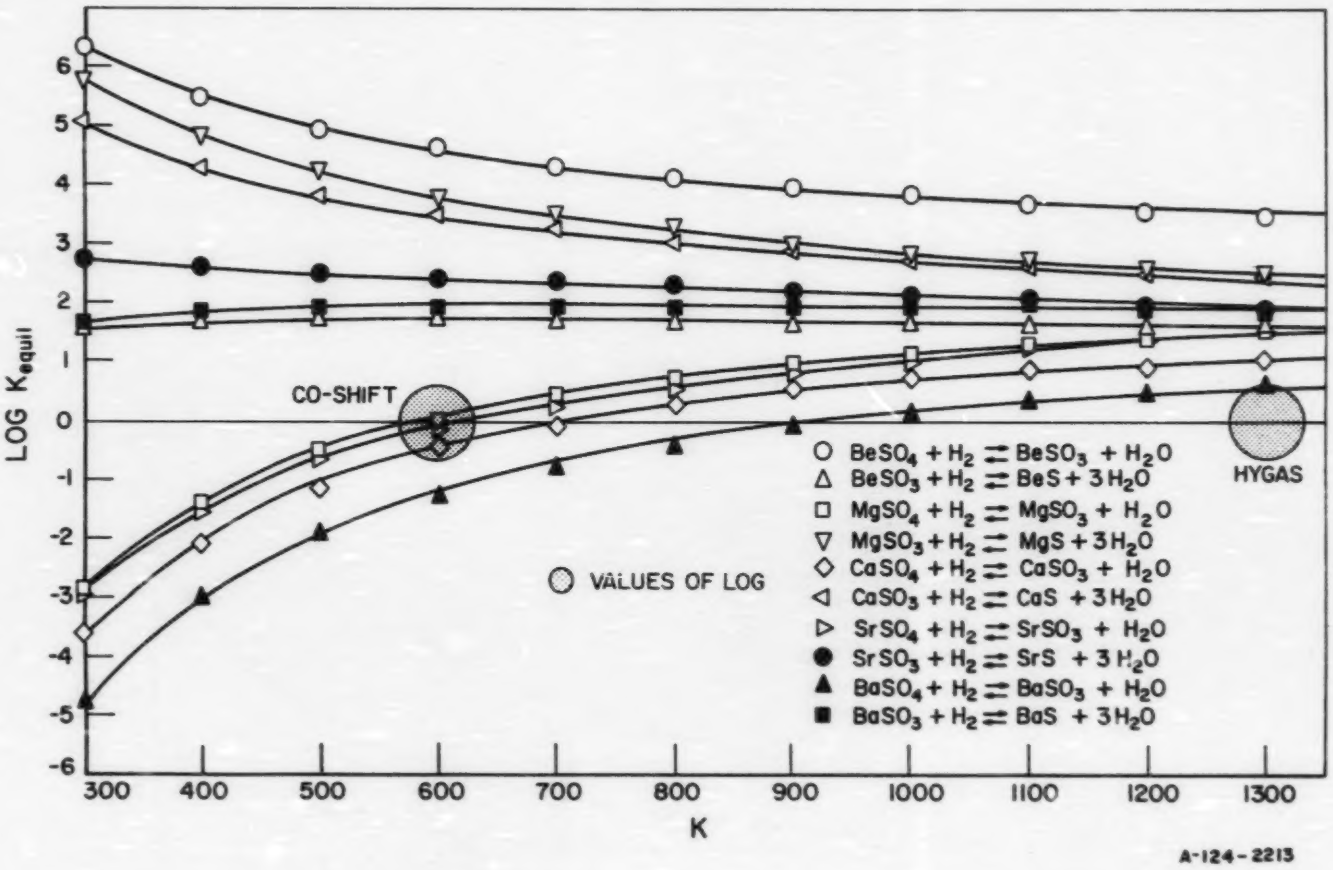

Figure E-10. REDUCTION REACTIONS OF SECOND-PERIOD SULFATES TO SULFITES TO SULFIDES

Values of Log $\left[(P_{H_2O})/(P_{H_2})\right]$ at 600 K = –0.07 (CO-Shift)
1300 K = –0.09 (HYGAS)
Log $\left[(P_{H_2O})^3/(P_{H_2})^3\right]$ at 600 K = –0.22 (CO-Shift)
1300 K = –0.28 (HYGAS)

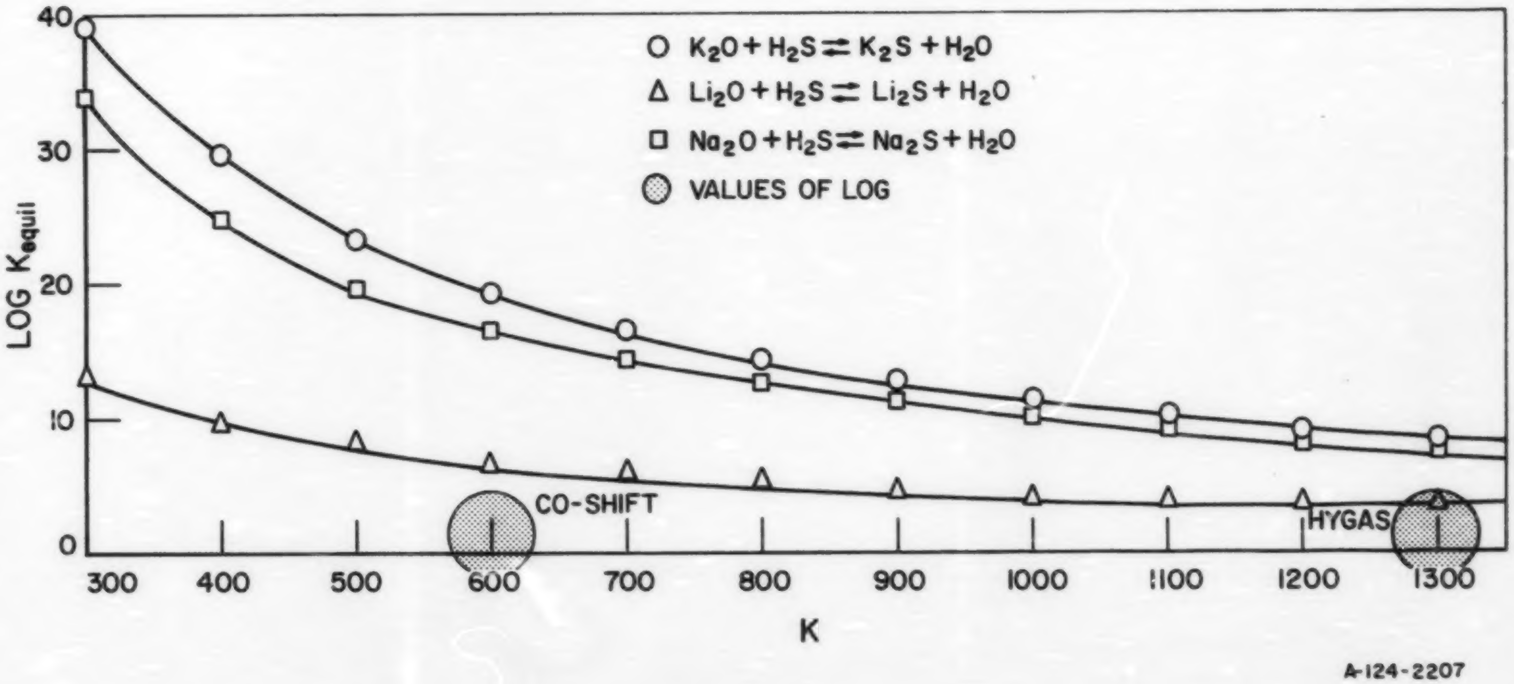

Figure E-11. SULFIDE FORMATION FROM FIRST-PERIOD OXIDES

Values of Log $\left[(P_{H_2O})/(P_{H_2S})\right]$ at 600 K = 1.35 (CO-Shift)
1300 K = 1.16 (HYGAS)

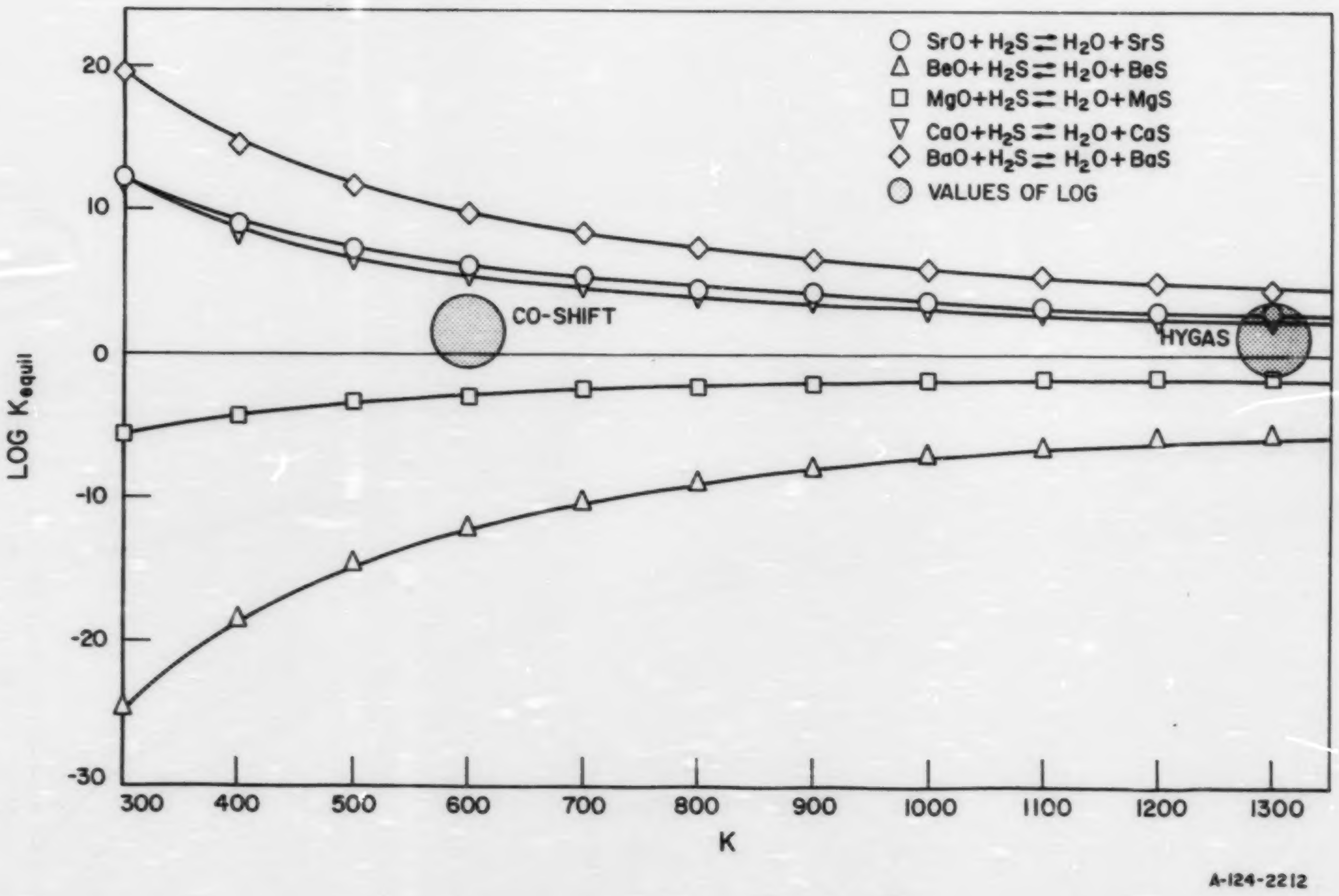

Figure E-12. SULFIDE FORMATION FROM SECOND-PERIOD OXIDES
Values of Log $\left[(P_{H_2O})/(P_{H_2S})\right]$ at 600 K = 1.35 (CO-Shift)
1300 K = 1.16 (HYGAS)

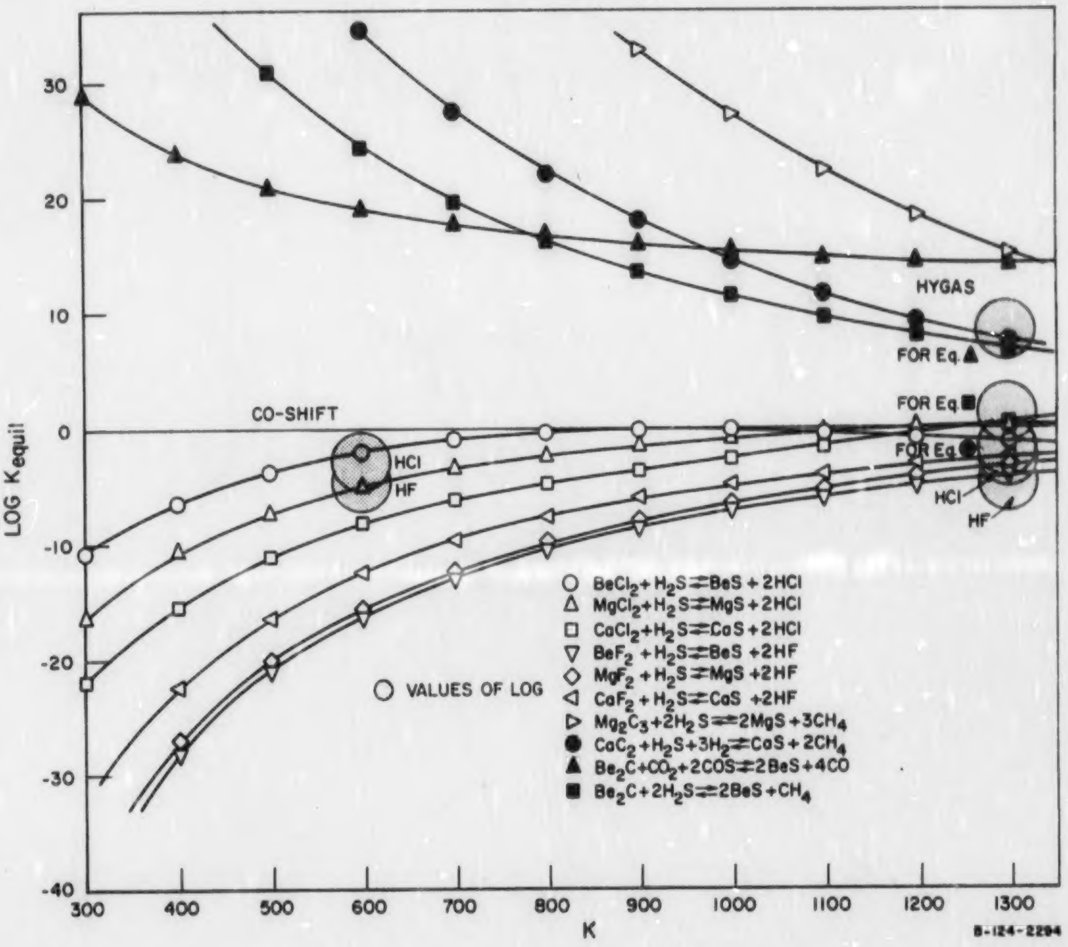

Figure E-13. SULFIDE FORMATION FROM SECOND-PERIOD CHLORIDES, FLUORIDES, AND CARBIDES

Assuming HCl = 500 ppm and HF = 50 ppm, the

Values of Log $\left[(P_{HCl})^2/(P_{H_2S})\right]$ at 600 K = –2.63 (CO-Shift)
1300 K = –2.67 (HYGAS)

Log $\left[(P_{HF})^2/(P_{H_2S})\right]$ at 600 K = –4.63 (CO-Shift)
1300 K = –4.67 (HYGAS)

For Eq. ▲ Log $\left[(P_{CO})^4/(P_{COS})^2(P_{CO_2})\right]$ at 1300 K = 8.02 (HYGAS)

For Eq. ■ Log $\left[(P_{CH_4})/(P_{H_2S})^2\right]$ at 1300 K = 0.99 (HYGAS)

For Eq. ● Log $\left[(P_{CH_4})^2/(P_{H_2})^3(P_{H_2S})\right]$ at 1300 K = –1.78 (HYGAS)

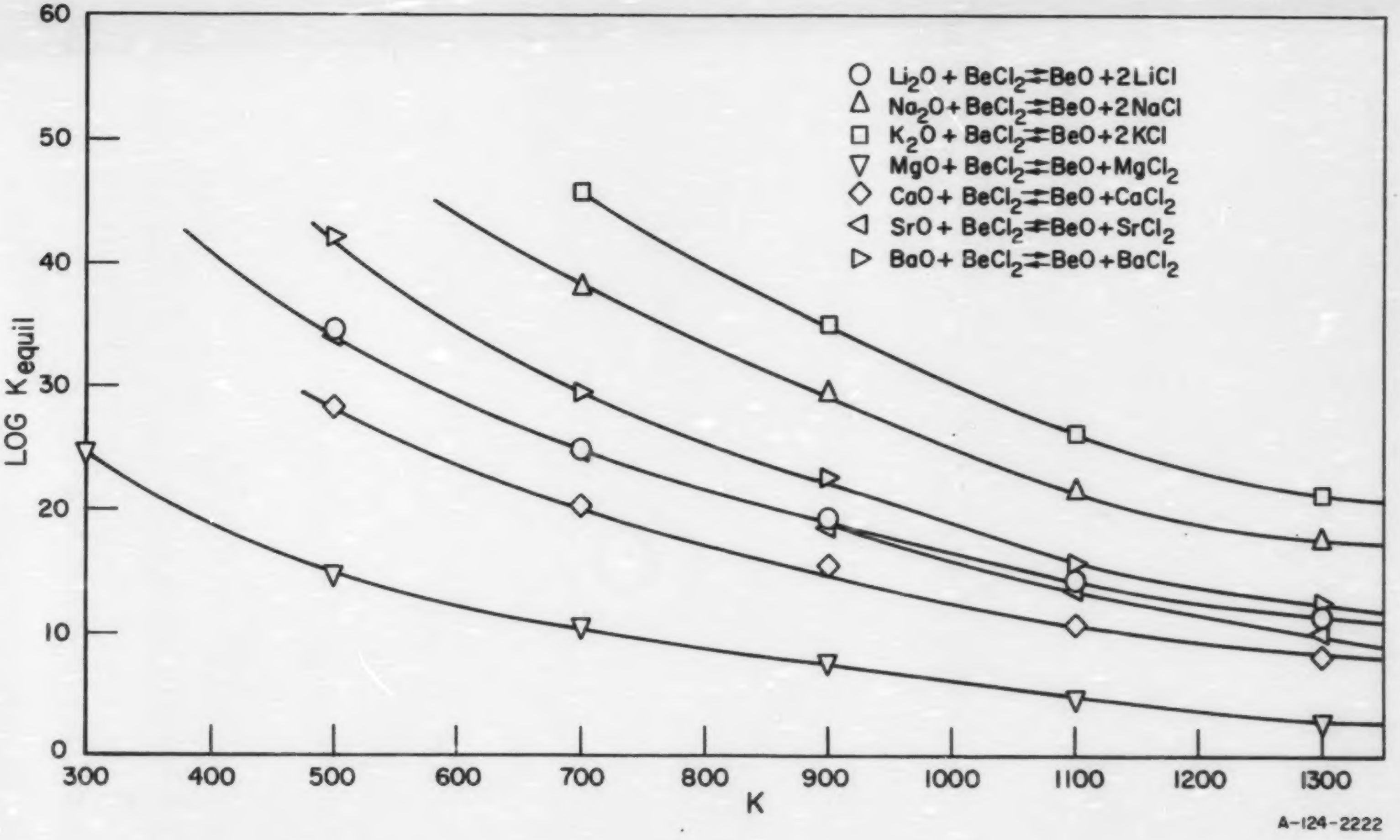

Figure E-14. FORMATION OF BeO FROM $BeCl_2$ AND FIRST- AND SECOND-PERIOD OXIDES

Note: Operating Regions (Log Values) are not calculated for solid-phase reactions such as these.

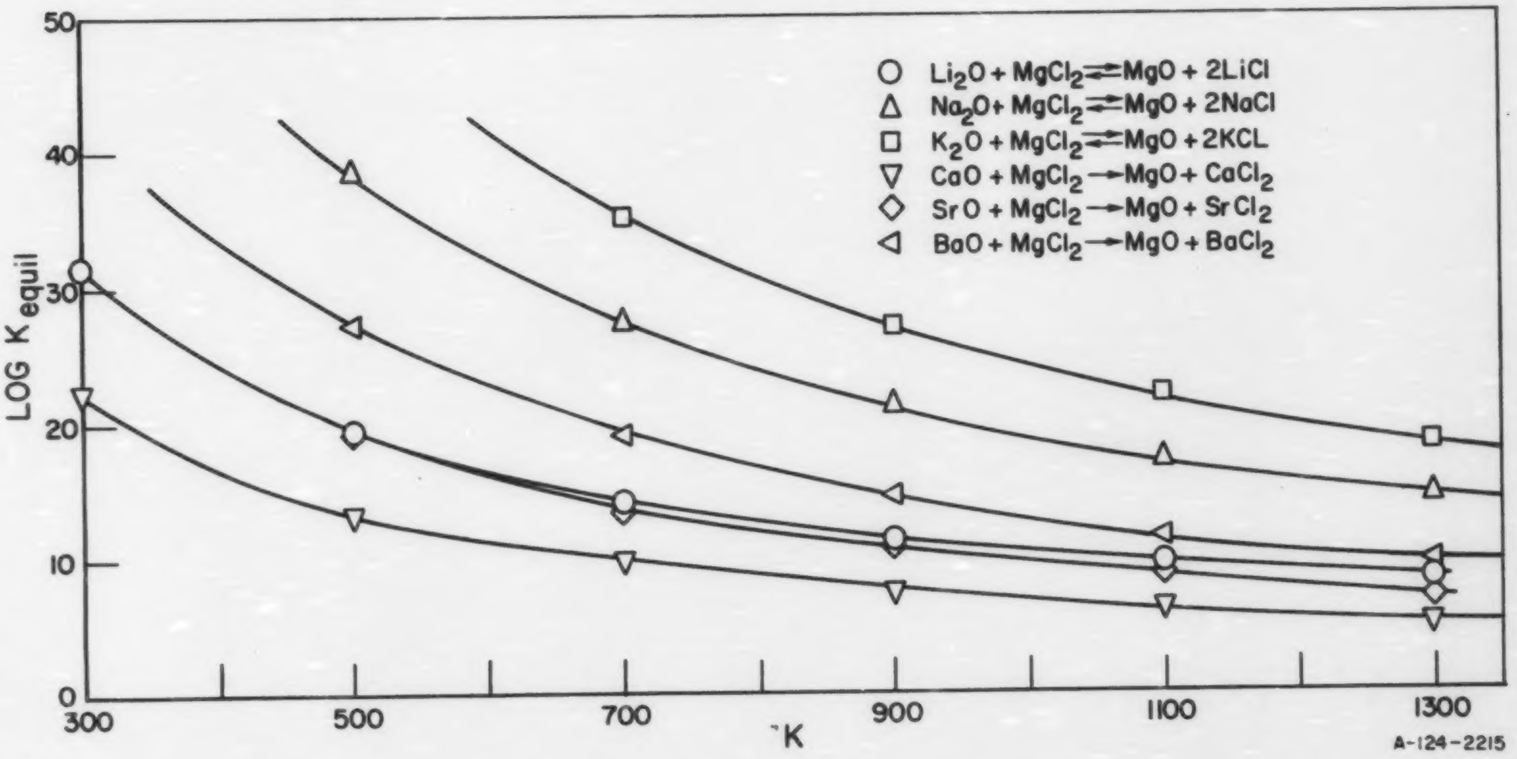

Figure E-15. FORMATION OF MgO FROM $MgCl_2$ AND FIRST- AND SECOND-PERIOD OXIDES

Note: Operating Regions (Log Values) are not calculated for solid-phase reactions such as these.

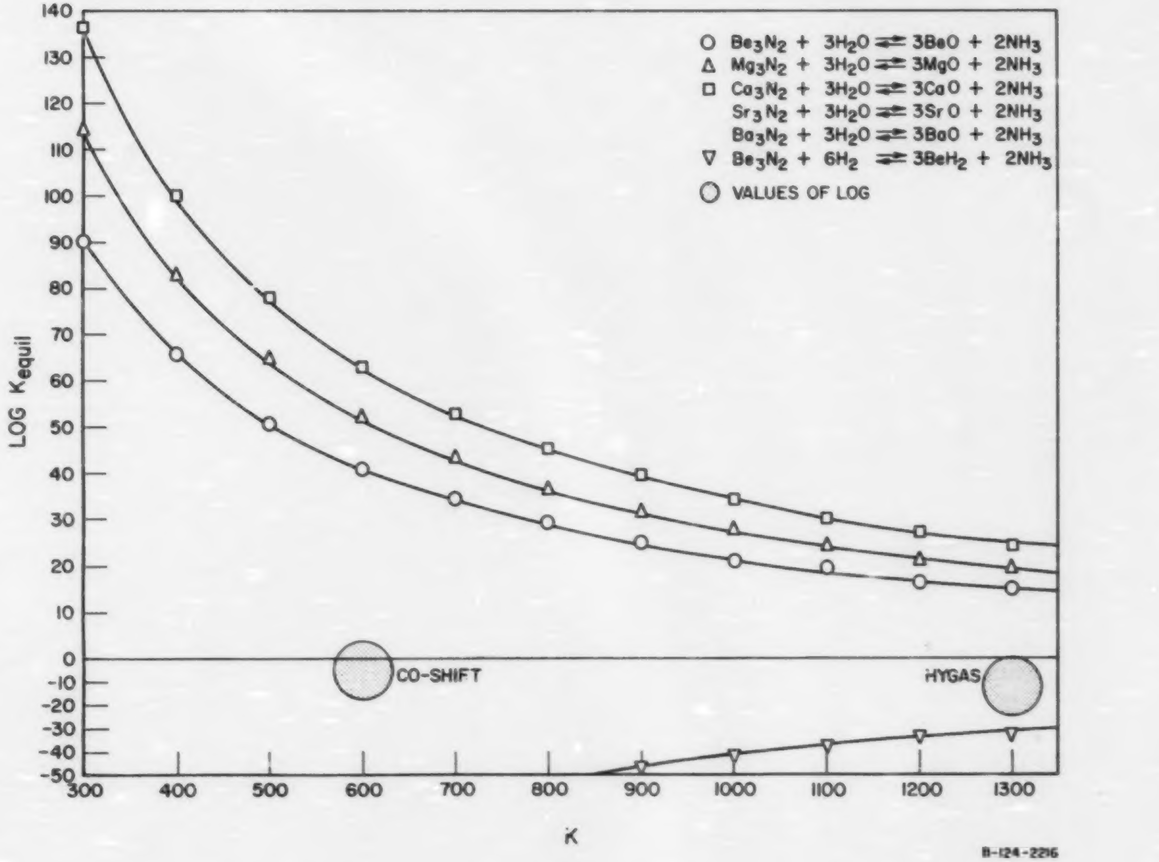

Figure E-16. HYDROLYSIS OF SECOND-PERIOD NITRIDES TO OXIDES AND NH_3 – HYDROGENATION OF Be_3N_2 TO BeH_2

For Eq.▽ , Assume BeH_2 = 1 ppm, the

Values of Log $\left[(P_{NH_3})^2(P_{BeH_2})^3/(P_{H_2})^6\right]$ at 1300 K = –12.43 (HYGAS)

Log $\left[(P_{NH_3})^2/(P_{H_2O})^3\right]$ at 600 K = –4.83 (CO-Shift)

1300 K = –4.20 (HYGAS)

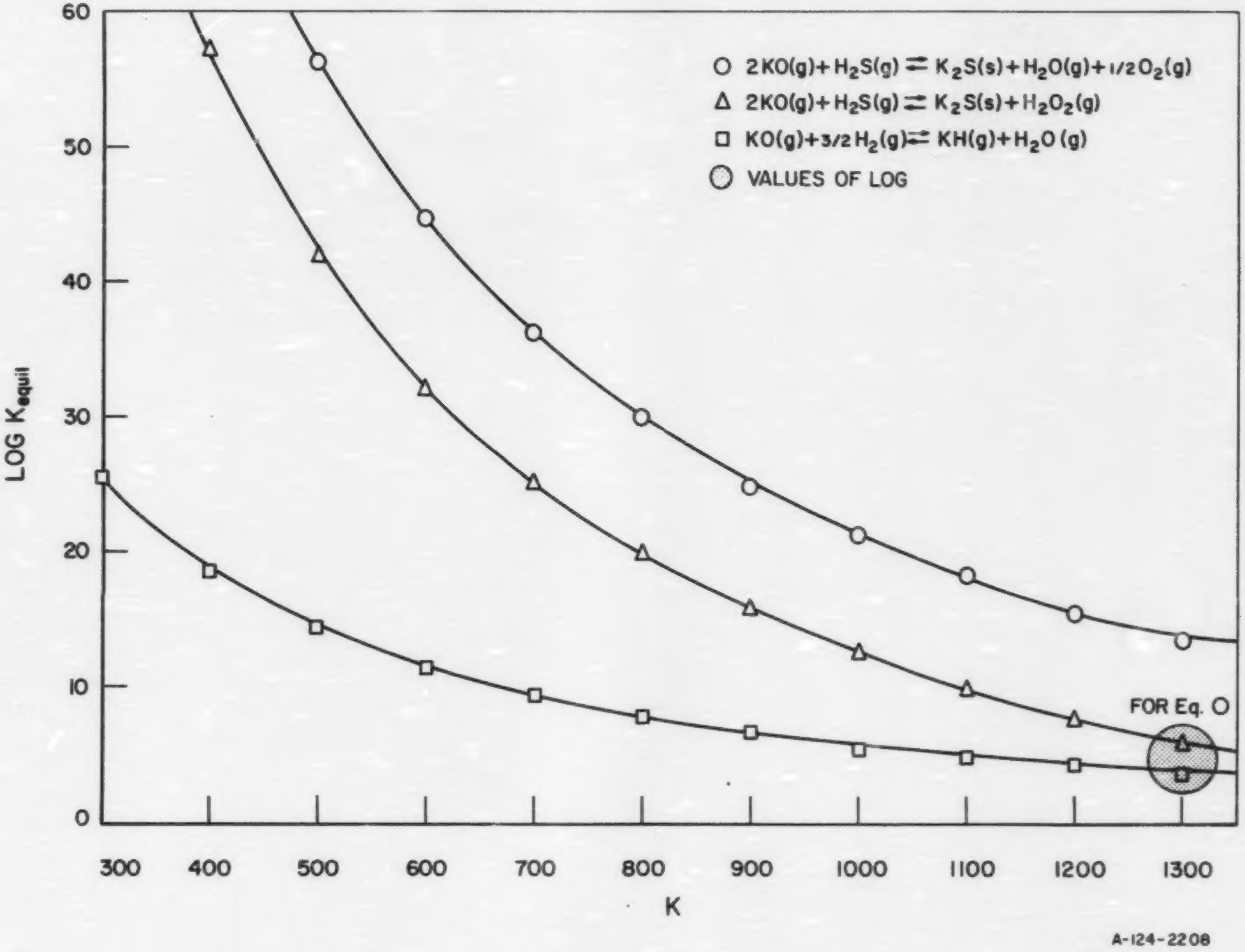

Figure E-17. MISCELLANEOUS REACTIONS INVOLVING KO (g)
Assuming KO = 1 ppm and O_2 = 0.01 ppb, the
Value of Log $\left[(P_{O_2})^{1/2}(P_{H_2O})/(P_{H_2S})(P_{KO})^2\right]$ at 1300 K = 4.66 (HYGAS)

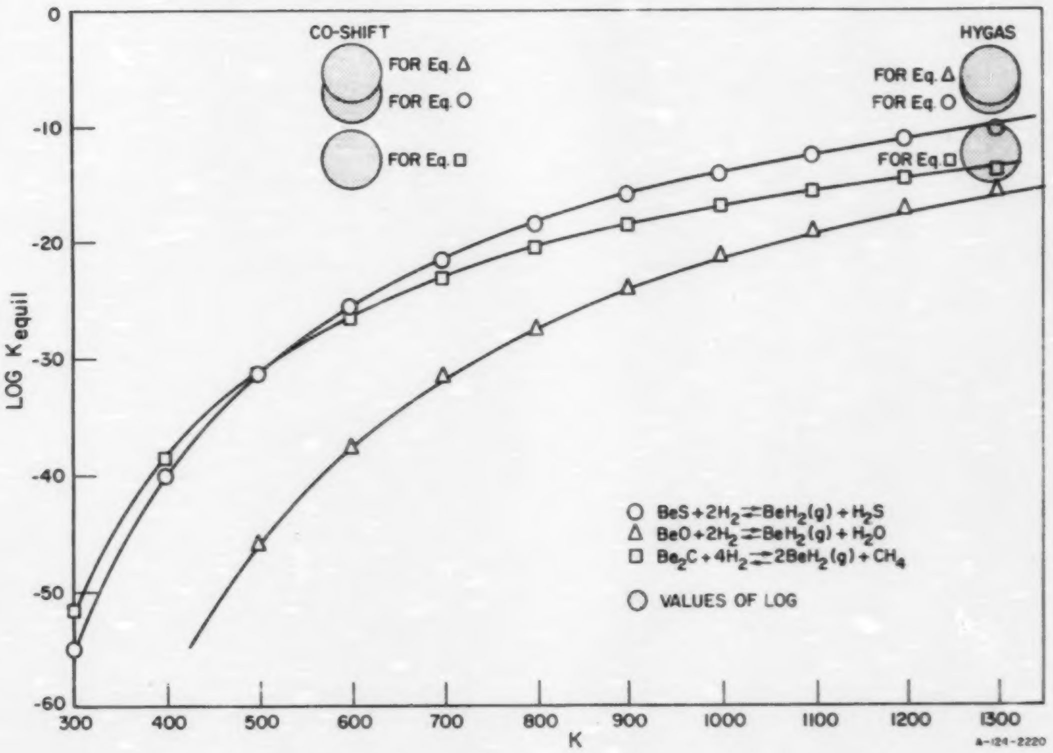

Figure E-18. HYDROGENATION OF BERYLLIUM COMPOUNDS FORMING BeH_2 (g)

Assuming BeH_2 = 1 ppm, the

Values of Log $\left[(P_{H_2S})(P_{BeH_2})/(P_{H_2})^2\right]$ at 600 K = –6. 88 (CO-Shift)
1300 K = –6. 57 (HYGAS) for Eq. ○

Log $\left[(P_{H_2O})(P_{BeH_2})/(P_{H_2})^2\right]$ at 600 K = –5. 53 (CO-Shift)
1300 K = –5. 41 (HYGAS) for Eq. △

Log $\left[(P_{CH_4})(P_{BeH_2})/(P_{H_2})^4\right]$ at 600 K = –12. 73 (CO-Shift)
1300 K = –12. 15 (HYGAS) for Eq. □

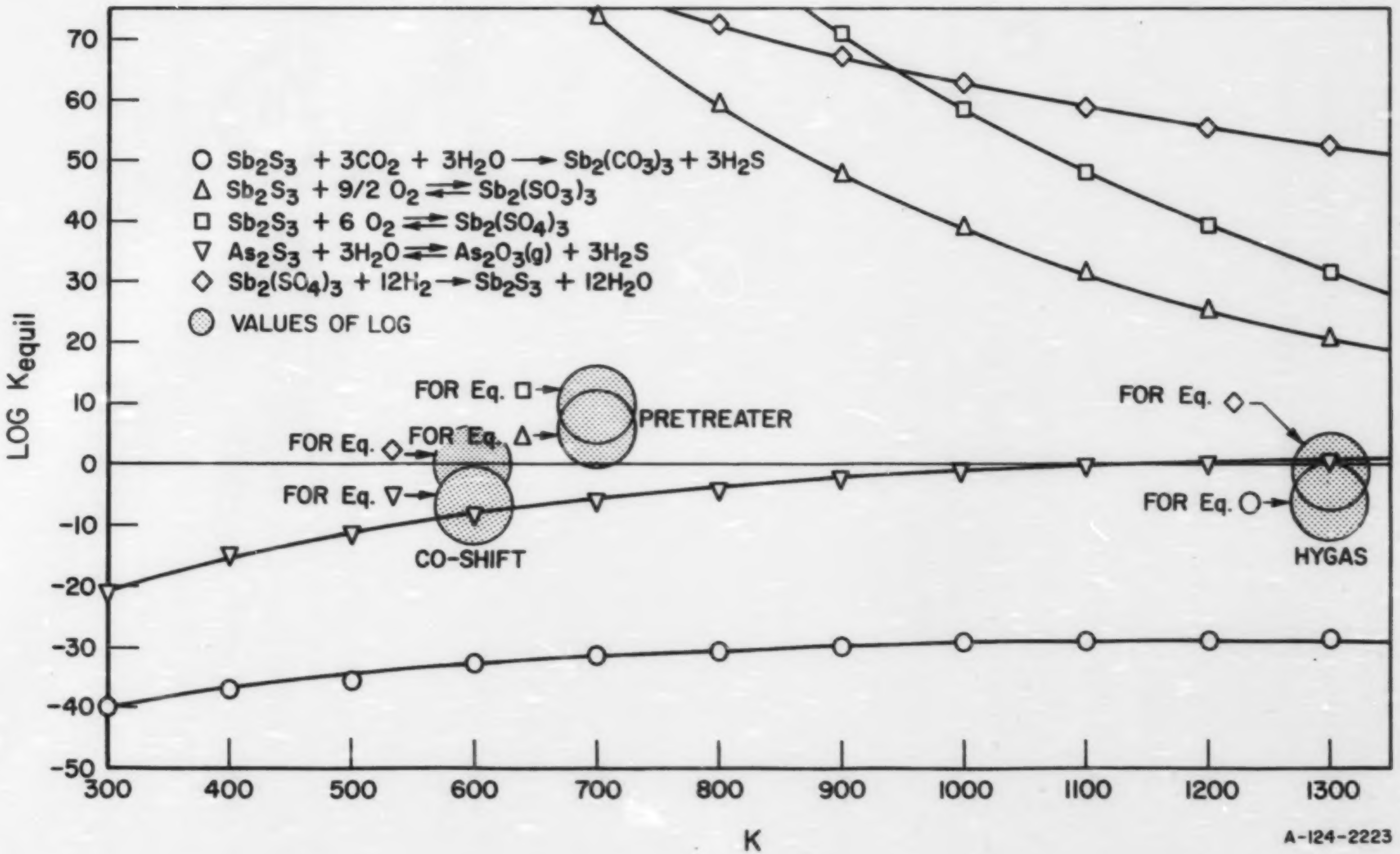

Figure E-19. MISCELLANEOUS REACTIONS OF ANTIMONY AND ARSENIC COMPOUNDS

The elevated pressures found in the hydrogasifier favor carbonate formation in these reactions. This follows from a consideration of the effect of pressure on reaction equilibrium for several situations which may be encountered:

1. $BeS + H_2O + CO_2 \rightleftarrows BeCO_3 + H_2S$ (Figure E-8)
2. $BeO + H_2S \rightleftarrows BeS + H_2O$ (Figure E-12)
3. $H_2O \rightleftarrows H_2 + 1/2\ O_2$
4. $MgCl_2 + Li_2O \rightleftarrows MgO + 2LiCl$ (Figure E-15)

In case 1, two moles of gas (H_2O, CO_2) will react to form one mole of gas (H_2S). Increasing the partial pressure of either H_2O or CO_2 (or decreasing P_{H_2S}), will push the reaction to the right. Decreasing the partial pressure of H_2O or CO_2 (or increasing H_2S or introducing inert gas), will pull the reaction to the left.

In case 2, one mole of H_2O will react to form one mole of H_2S. Variations in pressure will not affect the equilibrium conversion of this reaction.

In case 3, one mole of gas decomposes to form 1.5 moles of product gas. Increasing the partial pressure of H_2 or O_2 will force the equilibrium to the left.

In case 4, solid phase reactions are not affected by changes in system pressure. (See comments on Figures E-14 and E-15).

The effect of pressure can be similarly judged for the other reactions posed in this study.

Figures E-9 and E-10 show the steps of reduction for the first- and second-period sulfates. The reduced forms of these elements are stable with respect to the oxidized forms in the HYGAS reactor. In Figure E-9, the reduction of sulfate to sulfite is not favored, but the overall reaction of sulfate to sulfide is favored in the hydrogasifier.

Figures E-11 and E-12 attempt to tie the oxides and sulfides together in the hydrogen sulfide/water exchange reactions. In general, the sulfide form is preferred, except for beryllium and magnesium oxides.

In Figure E-13, various chloride, and some miscellaneous reactions are presented. Here it is assumed for calculational purposes, that 500 ppm of chlorine (as HCl) and 50 ppm of fluorine (as HF) exist in the HYGAS and CO-shift reactors at steady state. The chlorine levels for some lignite feeds may be this high in the raw gas from the hydrogasifier but much lower in the CO-shift reactor, depending upon removal efficiency during water quenching. These reactions go to products as indicated.

Figures E-14 and E-15 show that beryllium and magnesium oxides are thermodynamically favored in these solid-phase exchange reactions. This is evidenced by the high positive values for the log of the equilibrium constant (log K_{eq}) over the given temperature range.

The hydrolysis of nitride compounds is shown in Figure E-16. Figures E-17 and E-18 present some miscellaneous reactions involving potassium oxide (gas) and beryllium compounds. Figure E-19 contains some reactions of arsenic and antimony compounds. The oxidation of antimony sulfide proceeds readily in the pretreater while the sulfate is readily reduced in the hydrogasifier. Arsenous oxide (As_2O_3, gas) is thermodynamically stable with respect to its sulfide in the HYGAS unit. Arsenous sulfide (As_2S_3, liquid) is stable with respect to its oxide in the CO-shift reactor. Considering several other arsenic-related reactions, however, the metallic form (As°) predominates in all reaction units.

The calculations presented in Table E-1 comprise the thermodynamic operating conditions in each of the process units for selected reactions. The derivation of these values is presented and substantiated in Appendix F.

Table E-2 contains the results of computer and other calculations to determine the equilibrium constants for the elements in numerous reactions at various temperatures. Elements not considered in this table, because only limited thermodynamic data are available, include germanium, samarium, and ytterbium. Chlorine, fluorine, nitrogen, and sulfur are not directly presented because the reactions include them as chlorides, fluorides, ammonia, and sulfides.

Table E-1. CALCULATED VALUES OF OPERATING REGIONS*

Pretreater (700K)	[Parameter]	Log [ ]
$MS + 3/2\ O_2 \rightleftarrows MSO_3$	$[1/P_{O_2}{}^{3/2}]$**	1.02
$MSO_3 + 1/2\ O_2 \rightleftarrows MSO_4$	$[1/P_{O_2}{}^{1/2}]$	0.34
$MS + 2O_2 \rightleftarrows MSO_4$	$[1/P_{O_2}{}^{2}]$	1.36
$MS + 3/2\ O_2 \rightleftarrows MO + SO_2$	$[P_{SO_2}{}^{\dagger}/P_{O_2}{}^{3/2}]$	−1.14
$MO + CO_2 \rightleftarrows MCO_3$	$[1/P_{CO_2}{}^{\dagger}]$	1.20
$MSO_4 \rightleftarrows MO_2 + SO_2$	$[P_{SO_2}]$	−2.16

HTR, OG (1300K); CO-Shift (600K)		HYGAS	CO-Shift
$MS + H_2 \rightleftarrows M(s, g) + H_2S$	$[P_{H_2S}/P_{H_2}]$	−1.25	−1.25
$MO + H_2 \rightleftarrows M(s, g) + H_2O$	$[P_{H_2O}/P_{H_2}]$	−0.093	0.348
$MS + H_2O \rightleftarrows MO + H_2S$	$[P_{H_2S}/P_{H_2O}]$	−1.16	−1.60
$MS + CO_2 + H_2O \rightleftarrows MCO_3 + H_2S$	$[P_{H_2S}/P_{CO_2} \cdot P_{H_2O}]$	−2.33	−2.70
$MSO_3 + 3H_2 \rightleftarrows MS + 3H_2O$	$[P_{H_2O^3}/P_{H_2{}^3}]$	−0.280	1.04
$MSO_4 + 4H_2 \rightleftarrows MS + 4H_2O$	$[P_{H_2O^4}/P_{H_2{}^4}]$	−0.374	1.39
$MO + CO_2 \rightleftarrows MCO_3$	$[1/P_{CO_2}]$	−1.17	−1.097
$MO + 2HCl \rightleftarrows MCl_2 + H_2O$	$[P_{H_2O}/P_{HCl_2}]$	3.82	4.19
$MS + 2HCl \rightleftarrows MCl_2 + H_2S$	$[P_{H_2S}/P_{HCl_2}]$	2.67	2.59
$MD + 2HF \rightleftarrows MF_2 + H_2O$	$[P_{H_2O}/P_{HF^2}]$	5.82	6.19
$MS + 2HF \rightleftarrows MF_2 + H_2S$	$[P_{H_2S}/P_{HF^2}]$	4.67	4.59

* Bituminous Coal.

** 21% O_2 is in the pretreater air.

† Based on Pretreater off-gas composition Table 1, Part 3, Column D.

Table E-2, Part 1. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
Antimony, Sb_2S_3 (See Figure E-19.)											
$Sb_2S_3 + 9/2\ O_2 \rightleftarrows Sb_2O_3 + 3SO_2$							93.6				
$Sb_2S_3 + 3O_2 \rightleftarrows 2Sb(s) + 3SO_2$							54.933				
$Sb_2S_3 + 3O_2 \rightleftarrows 2Sb(g) + 3SO_2$							29.753				
$Sb_2S_3 + 3O_2 \rightleftarrows 1/2\ Sb_4(g) + 3SO_2$							51.348				
$Sb_2S_3 + 3H_2O \rightleftarrows Sb_2O + 3H_2S$						−9.241	−10.44	−12.041			
$Sb_2S_3 + 6HCl \rightleftarrows 2SbCl_3 + 3H_2S$						−3.723	− 3.888	− 4.148			
$Sb_2O_3 + 6HCl \rightleftarrows 2SbCl_3 + 3H_2O$				3.704			6.552	7.893			
$Sb + 3HCl \rightleftarrows SbCl_3 + 3/2\ H_2$				−1.758			− 0.8445	− 0.383			
$Sb(g) + 3HCl \rightleftarrows SbCl_3 + 3/2\ H_2$				5.609			11.746	12.092			
$Sb_4\ (g) + 12HCl \rightleftarrows 4SbCl_3 + 6H_2$				−1.967			3.792	8.136			
$Sb_2O_3 + 3H_2 \rightleftarrows 2Sb + 3H_2O$	6.238						9.399	8.659			
$Sb_2O_3 + 3H_2 \rightleftarrows 2Sb\ (g) + 3H_2O$				−1.915			−16.939	−22.987			
$Sb_2O_3 + 3H_2 \rightleftarrows 1/2\ Sb_4(g) + 3H_2O$				5.229			4.656	3.825			
$Sb_2S_3 + 3H_2 \rightleftarrows 2Sb + 3H_2S$						−1.354	− 2.199	− 3.382			
$Sb_2S_3 + 3H_2 \rightleftarrows 2Sb(g) + 3H_2S$						−21.7	−27.379	−35.028			
$Sb_2S_3 + 3H_2 \rightleftarrows 1/2\ Sb_4(g) + 3H_2S$						−4.019	− 5.784	− 8.216			
Arsenic, $FeS_2 \cdot FeAs_2$ (See Figure E-19.)											
$As + 3/2\ H_2 \rightleftarrows AsH_3(g)$						−5.222	− 5.752	− 6.484			
$As_2O_3 + 3H_2 \rightleftarrows 2As + 3H_2O$								10.683	13.858		
$As_2O_3 + 6H_2 \rightleftarrows 2AsH_3(g) + 3H_2O$								−2.285	−1.229		
$As_2O_3 + 6HCl \rightleftarrows 2AsCl_3 + 3H_2O$								−0.895	1.893		
$AsH_3 + 3HCl \rightleftarrows AsCl_3 + 3H_2$								0.72	1.561	2.948	
$As + 3HCl \rightleftarrows AsCl_3 + 3/2H_2$								5.764	−5.9825	−6.2765	
Barium (See Figures E-1 to E-4, E-7, E-8, E-10, E-12, and E-14 to E-16.)											
Beryllium (See Figures E-1 to E-4, E-7, E-8, E-10, E-12 to E-14, E-16 and E-18.)											
Bismuth, Bi_2S_3											
$Bi_2O_3 + 3H_2S \rightleftarrows Bi_2S_3 + 3H_2O$						15.004	17.749	21.047			
$Bi_2S_3 + 3H_2 \rightleftarrows 2Bi(g) + 3H_2S$				−6.309							
$Bi_2S_3 + 3H_2 \rightleftarrows 2Bi(\ell) + 3H_2S$				3.065			0.599	− 0.868			
$Bi_2O_3 + 3H_2 \rightleftarrows 2Bi(g) + 3H_2O$						2.584	0.4	− 2.585			
$Bi_2O_3 + 3H_2 \rightleftarrows 2Bi(\ell) + 3H_2O$						16.942	18.348	20.0			

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Table E-2, Part 2. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	1300	1200	1100	1000	900	800	700	600	500	400	298
	Temperature, K										
	log K_{eq}										
Boron, $B(OCH_3)_3$											
$B_2O_3 + 4HCl + H_2 \rightleftarrows 2BCl_2(g) + 3H_2O$	−22.471						−46.765	−55.96			
$B_2O_3 + 4HF + H_2 \rightleftarrows 2BF_2(g) + 3H_2O$	−13.951						−31.271	−37.924			
Calcium (See Figures E-1 to E-4, E-7, E-8, E-10, and E-12 to E-16.)											
Cadmium, CdS											
$CdS + 3/2\ O_2 \rightleftarrows CdO + SO_2$							26.036				
$CdS + O_2 \rightleftarrows Cd + SO_2$							12.203				
$CdS + 2O_2 \rightleftarrows CdSO_4$							39.805				
$CdS + H_2O \rightleftarrows CdO + H_2S$		− 5.204					− 8.644	−10.039			
$CdS + H_2O + CO_2 \rightleftarrows CdCO_3 + H_2S$	−30.393						−28.944	−28.634			
$CdO + CO_2 \rightleftarrows CdCO_3$		−25.003					−20.3	−18.595			
$CdS + 2HCl \rightleftarrows CdCl_2 + H_2S$		− 2.145					− 0.483	0.47			
$CdO + 2HCl \rightleftarrows CdCl_2 + H_2O$		3.059					8.161	10.509			
$Cd + H_2S \rightleftarrows CdS + H_2$	1.597						6.841	8.434			
$Cd + 1/2\ O_2 \rightleftarrows CdO$								13.833			
$CdSO_4 + 4H_2 \rightleftarrows CdS + 4H_2O$		16.212					22.739	25.199			
Chlorine											
Chromium											
Cobalt, CoS											
$CoSO_4 + 4H_2 \rightleftarrows CoS + 4H_2O$				17.072			22.144	24.791			
$CoS + H_2O \rightleftarrows CoO + H_2S$	−1.872						− 4.349	− 5.223			
$CoO + 2HCl \rightleftarrows CoCl_2 + H_2O$	−0.168						3.226	4.805			
$CoS + 2HCl \rightleftarrows CoCl_2 + H_2S$	−2.04						− 1.123	− 0.418			
Copper, CuS											
$CuS + 2O_2 \rightleftarrows CuSO_4$							34.731				
$Cu_2S + 5/2\ O_2 \rightleftarrows CuSO_4 + CuO$							37.683				
$CuS + 3/2\ O_2 \rightleftarrows CuO + SO_2$							25.746				
$CuSO_4 + 4H_2 \rightleftarrows CuS + 4H_2O$							27.813	31.117			
$CuSO_4 + 4CO \rightleftarrows CuS + 4CO_2$							31.517	48.697			
$CuS + H_2 \rightleftarrows Cu(s) + H_2S$	0.484							− 0.426			
$CuS + H_2O \rightleftarrows CuO + H_2S$	−4.912							−10.363			
$Cu_2S + H_2 \rightleftarrows 2Cu(s) + H_2S$	−2.758							− 4.579			
$Cu_2S + H_2O \rightleftarrows Cu_2O + H_2S$	−6.821							−12.404			
$CuO + H_2 \rightleftarrows Cu + H_2O$	5.396										

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Table E-2, Part 3. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
$2CuO + H_2S + H_2 \rightleftarrows Cu_2S + 2H_2O$	6.775							12.227			
$Cu_2O + H_2 \rightleftarrows 2Cu + H_2O$	− 0.075							0.314			
$Cu_2S + H_2S \rightleftarrows 2CuS + H_2$	− 3.726							− 3.727			
$Cu_2S + 2HCl \rightleftarrows 2CuCl + H_2S$	− 4.293							− 3.449			
$Cu_2S + 2HF \rightleftarrows 2CuF + H_2S$	−20.103							−51.785			
$Cu_2S + 4HCl \rightleftarrows 2CuCl_2 + H_2 + H_2S$							−17.872	−18.055			
$Cu_2S + 4HF \rightleftarrows 2CuF_2 + H_2 + H_2S$							−21.446	−21.987			
Fluorine											
Germanium											
Iron, $FeCO_3$, FeS_2, FeO											
$FeS_2 + 3O_2 \rightleftarrows FeSO_4 + SO_2$							62.523	75.636			
$FeS_2 + O_2 \rightleftarrows FeS + SO_2$							19.308	21.899			
$FeS_2 + 5/2\ O_2 \rightleftarrows FeO + 2SO_2$							50.845	59.425			
$2FeS_2 + 11/2\ O_2 \rightleftarrows Fe_2O_3 + 4SO_2$							57.78	68.102			
$3FeS_2 + 8O_2 \rightleftarrows Fe_3O_4 + 6SO_2$							55.959	65.776			
$FeCO_3 \rightleftarrows FeO + CO_2$							3.976	2.963			
$2FeCO_3 + 1/2\ O_2 \rightleftarrows Fe_2O_3 + 2CO_2$							10.816	11.641			
$FeS_2 + H_2 \rightleftarrows FeS + H_2S$							0.264	− 0.551			
$FeS + H_2 \rightleftarrows Fe + H_2S$	− 2.267						− 4.343	− 5.108			
$FeS + H_2O \rightleftarrows FeO + H_2S$	− 1.814						− 3.143	− 3.618			
$FeS + H_2O + CO_2 \rightleftarrows FeCO_3 + H_2S$							−12.571	−12.356			
$FeS_2 + H_2 + H_2O + CO_2 \rightleftarrows FeCO_3 + 2H_2S$							−19.552	−20.025			
$FeS + 2HCl \rightleftarrows FeCl_2 + H_2S$	− 2.325						− 0.089	1.009			
$FeS_2 + 4HCl \rightleftarrows FeCl_3(g) + 2H_2S + 1/2\ Cl_2$							−15.589	−18.651			
$FeS + 2HF \rightleftarrows FeF_2 + H_2S$	− 8.457						− 5.651	− 4.674			
$FeS_2 + 4HF \rightleftarrows FeF_3(g) + 2H_2S + 1/2\ F_2$							−26.584	−31.459			
$FeO + 2HCl \rightleftarrows FeCl_2 + H_2O$	− 0.512						3.054	4.627			
$FeO + 2HF \rightleftarrows FeF_2(g) + H_2O$	− 5.437						−11.42	−13.527			
$FeO + 3HCl \rightleftarrows FeCl_3(g) + H_2O + 1/2\ H_2$	− 3.758						− 5.341	− 5.959			
$Fe + 1/2\ O_2 \rightleftarrows FeO$							16.836				
$FeSO_4 + 4H_2 \rightleftarrows FeS + 4H_2O$							19.224	21.037			
$Fe_2O_3 + 2H_2S + H_2 \rightleftarrows 2FeS + 3H_2O$	6.237						8.041	8.573			

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Table E-2, Part 4. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

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	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
Lead, PbS											
$PbS + 2O_2 \rightleftarrows PbSO_4$	14.987						42.731	52.913			
$PbS + 3/2\ O_2 \rightleftarrows PbO(g) + SO_2$							15.469				
$PbS + O_2 \rightleftarrows Pb + SO_2$							15.445				
$PbS + H_2O + CO_2 \rightleftarrows PbCO_3 + H_2S$	−31.133						−30.267	−30.142			
$PbO + CO_2 \rightleftarrows PbCO_3$	−26.716						−22.078	−20.676			
$PbS + H_2O \rightleftarrows PbO(g) + H_2S$	− 6.697						−19.212	−23.754			
$PbS + H_2O \rightleftarrows PbO(s) + H_2S$	− 4.417						− 8.189	− 9.466			
$PbS + H_2 \rightleftarrows Pb(l) + H_2S$	− 0.998						− 3.599	− 4.584			
$PbS + 3/2\ H_2 \rightleftarrows PbH(g) + H_2S$	− 6.404						−16.737	−20.552			
$PbS + 2HCl \rightleftarrows PbCl_2(g) + H_2S$	− 1.197						0.809	1.974			
$PbS + 2HF \rightleftarrows PbF_2 + H_2S$	− 3.157						− 2.018	− 1.418			
$PbS + 3/2\ O_2 \rightleftarrows PbO(s) + SO_2$							26.491				
$PbSO_4 + 4H_2 \rightleftarrows PbS + 4H_2O$	13.395						19.813	21.861			
$Pb + 1/2\ O_2 \rightleftarrows PbO(g)$							0.023				
$PbO(s) \rightleftarrows PbO(g)$	− 2.37						−11.023	−14.288			
$Pb + 1/2\ O_2 \rightleftarrows PbO(s)$	3.677						11.046	13.811			
Lithium (See Figures E-5, E-6, E-9, E-11, E-14, and E-15.)											
Magnesium (See Figures E-1 to E-4, E-7, E-8, E-10, and E-12 to E-16.)											
Manganese $MnCO_3$, MnO_2											
$MnCO_3 + H_2S \rightleftarrows MnS + CO_2 + H_2O$							4.962	4.181			
$MnCO_3 \rightleftarrows MnO + CO_2$							1.027	− 0.384			
$MnO + H_2S \rightleftarrows MnS + H_2O$	2.167						3.935	4.565			
$MnSO_4 + 4H_2 \rightleftarrows MnS + 4H_2O$					16.202		18.592	20.286			
$MnCO_3 + 2HCl \rightleftarrows MnCl_2 + H_2O + CO_2$							6.073	6.554			
$MnO + 2HCl \rightleftarrows MnCl_2 + H_2O$	0.54						5.042	6.938			
$MnCO_3 + 2HF \rightleftarrows MnF_2 + H_2O + CO_2$							2.671	2.622			
$MnO + 2HF \rightleftarrows MnF_2 + H_2O$	− 1.918						1.64	3.006			
$MnS + 2HCl \rightleftarrows MnCl_2 + H_2S$	− 1.627						1.107	2.373			
$MnS + 2HF \rightleftarrows MnF_2 + H_2S$	− 4.085						− 2.295	− 1.559			

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Table E-2, Part 5. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
Mercury, Hg, HgS											
$HgS + 3/2\ H_2 \rightleftarrows HgH + H_2S$							−13.26	−16.57			
$HgO + H_2S \rightleftarrows HgS + H_2O$							8.835	16.182			
$Hg(g) + 1/2\ H_2 \rightleftarrows HgH(g)$	− 8.28						−14.35	−16.783			
$HgS + H_2O \rightleftarrows HgO(g) + H_2S$							−15.147	−19.08			
$HgS + 2HF \rightleftarrows HgF_2(g) + H_2S$							−17.244	−19.216			
$HgS + 2HCl \rightleftarrows HgCl_2 + H_2S$							− 3.502	− 4.381			
$HgO(g) + 2HF \rightleftarrows HgF_2 + H_2O$	− 4.403						− 2.097	− 0.138			
$HgO(g) + 2HCl \rightleftarrows HgCl_2 + H_2O$	3.225						11.645	14.697			
$HgS + O_2 \rightleftarrows Hg + SO_2$							20.134				
$HgS + 3/2\ O_2 \rightleftarrows HgO(g) + SO_2$							19.545				
$HgS + 3/2\ O_2 \rightleftarrows HgO(s) + SO_2$							20.845				
$HgO(s) \rightleftarrows Hg(g) + 1/2\ O_2$							− 0.711				
$HgO(g) \rightleftarrows Hg(g) + 1/2\ O_2$							0.601				
$HgO(s) \rightleftarrows HgO(g)$							− 1.312				
$Hg + 1/2\ O_2 \rightleftarrows HgO(g)$							− 0.601				
$HgO(s) + 2HF \rightleftarrows HgF_2 + H_2O$							− 3.47	− 3.034			
$HgO(s) + 2HCl \rightleftarrows HgCl_2 + H_2O$							10.333	11.801			
$HgS + H_2 \rightleftarrows Hg(g) + H_2S$	2-3						1.05	0.213			
$HgO(s) + H_2 \rightleftarrows Hg + H_2O$							14.925	16.395			
$HgF_2 + H_2 \rightleftarrows Hg(g) + 2HF$	13.79						18.334	19.429			
$HgCl_2 + H_2 \rightleftarrows Hg(g) + 2HCl$	5.162						4.592	4.594			
Molybdenum, MO_2S_3											
$Mo_2S_3 + 6H_2O \rightleftarrows 2MoO_3 + 3H_2S + 3H_2$							−25.836	−29.553			
$MoS_2 + 2H_2O \rightleftarrows MoO_2 + 2H_2S$							−18.61	−20.385			
$MoS_3 + 3H_2O \rightleftarrows MoO_3 + 3H_2S$							− 9.904	−12.151			
$Mo_2S_3 + 3H_2O \rightleftarrows 2MoO + 3H_2S + 1/2\ O_2$							−110.316	−132.843			
$Mo_2S_3 + 4H_2O \rightleftarrows 2MoO_2 + 3H_2S + H_2$							−57.781	−66.28			

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Table E-2, Part 6. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
Nickel, NiS, $NiCO_3$, Ni_3S_2											
$Ni + 1/2\ O_2 \rightleftarrows NiO$							13.147				
$Ni_3S_2 + 7/2\ O_2 \rightleftarrows 3NiO + 2SO_2$							70.716				
$Ni_3S_2 + 9/2\ O_2 \rightleftarrows 2NiSO_4 + NiO$							93.674				
$NiS + 2O_2 \rightleftarrows NiSO_4$								48.748			
$NiSO_4 + 4H_2 \rightleftarrows NiS + 4H_2O$								24.342			
$3NiSO_4 + 13H_2 \rightleftarrows Ni_3S_2 + 12H_2O + H_2S$				50.235			63.436	70.127			
$NiO + H_2S \rightleftarrows NiS + H_2O$								6.431			
$NiO + H_2 \rightleftarrows Ni + H_2O$	2.083						2.489	2.591			
$Ni_3S_2 + 3H_2O \rightleftarrows 3NiO + 2H_2S + H_2$				−10.137			−14.278	−16.394			
$NiO + CO_2 \rightleftarrows NiCO_3$											−17.086
$Ni_3S_2 + 2H_2 \rightleftarrows 3Ni + 2H_2S$				− 3.369			− 6.811	− 8.621			
$Ni + H_2S \rightleftarrows NiS + H_2$								3.843			
$NiS + 2HF \rightleftarrows NiF_2 + H_2S$								− 3.169			
$NiS + 2HCl \rightleftarrows NiCl_2 + H_2S$								− 2.293			
$NiO + 2HF \rightleftarrows NiF_2 + H_2O$	− 1.883						1.881	3.262			
$NiO + 2HCl \rightleftarrows NiCl_2 + H_2O$	− 1.132						2.61	4.138			
$Ni_3S_2 + 6HF \rightleftarrows 3NiF_2 + 2H_2S + H_2$							− 8.635	− 6.608			
$Ni_3S_2 + 6HCl \rightleftarrows 3NiCl_2 + 2H_2S + H_2$							− 6.448	− 3.58			
$3NiS \rightleftarrows Ni_3S_2 + S$								− 6.606			
$NiS + CO_2 + H_2O \rightleftarrows NiCO_3 + H_2S$											−29.988
Nitrogen, Organic											
Potassium (See Figures E-5, E-6, E.9, E-11, E-14, E-15, E-17)											
Samarium											
Selenium, SeS, $FeSe_2$											
$Se + H_2 \rightleftarrows H_2Se(g)$					− 0.022		− 0.174	− 0.328			
$Se_2(g) + 2H_2 \rightleftarrows 2H_2Se(g)$					0.844		2.535	3.782			
$Se + 6HF \rightleftarrows SeF_6 + 3H_2$					−51.665		−57.781	−62.338			
$Se_2(g) + 12HF \rightleftarrows 2SeF_6 + 6H_2$					−97.844		−112.805	−123.895			
$SeH_2 + 6HF \rightleftarrows SeF_6 + 4H_2$					−59.993		−67.561	−73.238			
Silicon, SiO_2											
$SiO_2(s) \rightleftarrows SiO(g) + 1/2\ O_2$		−18.749					−46.346				
$SiO_2 + 2H_2S \rightleftarrows 2H_2O + SiS_2(s)$	−10.43						−19.306	−22.509			
$SiO_2 + 2H_2 \rightleftarrows Si(s) + 2H_2O$	−13.066						−27.19	−32.39			
$SiO_2 + 4H_2 \rightleftarrows SiH_4(g) + 2H_2O$	−19.034						−33.838	−39.312			
$SiO_2 + H_2S + H_2 \rightleftarrows SiS(g) + 2H_2O$	−11.91						−30.984	−37.977			
$SiO_2 + 4HF \rightleftarrows SiF_4 + 2H_2O$	− 0.367						3.564	4.933			
$SiO_2 + 4HCl \rightleftarrows SiCl_4(g) + 2H_2O$	− 9.896						−14.495	−16.193			

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Table E-2, Part 7. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
Silver, Ag, AgS											
$2Ag + 1/2\ O_2 \rightleftarrows Ag_2O$							0.59	0.536	− 0.237		
$2Ag + H_2S \rightleftarrows Ag_2S + H_2$							− 2.263	0.312			
$Ag_2S + 2O_2 \rightleftarrows Ag_2SO_4$							30.203	33.862			
$Ag_2SO_4 + 4H_2 \rightleftarrows Ag_2S + 4H_2O$									2.061		
$Ag_2O + 2HF \rightleftarrows 2AgF + H_2O$									23.469		
$Ag_2O + 2HCl \rightleftarrows 2AgCl + H_2O$							−17.395	−19.17			
$Ag_2S + 2HF \rightleftarrows 2AgF + H_2S$							− 2.077	− 1.32			
$Ag_2S + 2HCl \rightleftarrows 2AgCl + H_2S$											−15.298
$Ag_2O + CO_2 \rightleftarrows Ag_2CO_3$											−62.176
$Ag_2S + H_2O + CO_2 \rightleftarrows Ag_2CO_3 + H_2S$									23.705		
$Ag_2O + H_2S \rightleftarrows Ag_2S + H_2O$								− 0.536			
$Ag_2S + H_2 \rightleftarrows 2Ag + H_2S$			− 0.918					0.992			
$AgCl + 1/2\ H_2 \rightleftarrows HCl + Ag$	1.119						8.403	9.317			
$AgF + 1/2\ H_2 \rightleftarrows HF + Ag$											
Sodium (See Figures E-5, E-6, E-9, E-11, E-14, E-15)											
Strontium (See Figures E-1 to E-4, E-7, E-8, E-10, and E-12 to E-16.)											
Sulfur											
Tellurium, $FeTe_2$, TeS											
$Te + O_2 \rightleftarrows TeO_2$		4.949					15.763	19.033			
$Te(g) + O_2 \rightleftarrows TeO_2$		7.371					23.563	29.236			
$Te_2(g) + 2O_2 \rightleftarrows 2TeO_2$		10.218					35.545	44.081			
$Te(s) + 6HF \rightleftarrows TeF_6(g) + 3H_2$		−30.112					−38.011	−41.301			
$Te(g) + 6HF \rightleftarrows TeF_6(g) + 3H_2$	−27.37						−30.211	−31.098			
$Te_2(g) + 12HF \rightleftarrows 2TeF_6 + 6H_2$	−58.5						−72.003	−76.587			
$Te + 4HCl \rightleftarrows TeCl_4 + 2H_2$		−13.73					−18.416	−19.828			
$Te(g) + 4HCl \rightleftarrows TeCl_4 + 2H_2$	−11.351						−10.616	− 9.625			
$Te_2(g) + 8HCl \rightleftarrows 2TeCl_4 + 4H_2$	−26.462						−32.813	−33.641			
$TeO_2 + 6HF \rightleftarrows TeF_6 + 2H_2O + H_2$		−19.196					−22.502	−22.947			
$TeO_2 + 4HCl \rightleftarrows TeCl_4 + 2H_2O$		− 2.814					− 2.907	− 1.478			
$TeO_2 + 3H_2 \rightleftarrows TeH_2 + 2H_2O$										15.154	
Tin, $SnCO_3$, SnS_2, SnS											
$SnS + 3/2\ O_2 \rightleftarrows SnO + SO_2$							31.111	37.039			
$SnS + 2O_2 \rightleftarrows SnO_2 + SO_2$							48.615	57.161			
$SnS_2 + 5/2\ O_2 \rightleftarrows SnO + 2SO_2$							50.45	59.394			
$SnS_2 + 3O_2 \rightleftarrows SnO_2 + 2SO_2$							73.211	85.386			

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Table E-2, Part 8. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
$SnS + H_2O \rightleftarrows SnO + H_2S$	− 2.295						− 3.569	− 4.105			
$SnS + H_2 \rightleftarrows Sn(\ell) + H_2S$	− 1.274						− 3.991	− 5.101			
$SnS_2 + H_2 \rightleftarrows SnS + H_2S$	~ 1						0.295	− 0.095			
$SnS_2 + O_2 \rightleftarrows SnS + SO_2$							19.331	22.355			
$SnO + 1/2\ O_2 \rightleftarrows SnO_2$							17.504	20.173			
$SnS + 2HCl \rightleftarrows SnCl_2(g) + H_2S$	− 1.627						− 1.609	− 1.167			
$SnS + 4HCl \rightleftarrows SnCl_4(g) + H_2S + H_2$	~ − 6						− 5.56	− 5.362			
$SnS_2 + 2HCl + H_2 \rightleftarrows SnCl_2 + 2H_2S$	− 1.39						− 1.314	− 1.262			
$SnS_2 + 4HCl \rightleftarrows SnCl_4 + 2H_2S$							− 5.265	− 5.457			
$SnS_2 + H_2 + H_2O \rightleftarrows SnO + 2H_2S$	− 1.513						− 3.274	− 4.200			
$SnS_2 + 2H_2O \rightleftarrows SnO_2 + 2H_2S$	− 2.033						− 1.406	− 2.771			
$SnO + H_2O \rightleftarrows SnO_2 + H_2$	− 0.52						1.868	1.429			
$Sn + H_2O \rightleftarrows SnO + H_2$	− 1.021							0.996			
$Sn + CO_2 \rightleftarrows SnO + CO$	− 0.741							0.399			
Titanium, TiO_2											
$TiO_2 + 2H_2S \rightleftarrows TiS_2 + 2H_2O$							−12.547	−14.651			
$TiO_2 \rightleftarrows TiO + 1/2\ O_2$	−11.682						−26.34	−31.629			
$TiO_2 + 2H_2 \rightleftarrows Ti + 2H_2O$	−14.259						−29.609	−35.225			
$TiO_2 + HCl + 1/2\ H_2 \rightleftarrows TiOCl(g) + H_2O$	−14.852						−33.450	−40.228			
$TiO_2 + 2HCl \rightleftarrows TiOCl_2(g) + H_2O$	− 9.595						−21.121	−25.328			
$TiO_2 + HF + 1/2\ H_2 \rightleftarrows TiOF(g) + H_2O$	−14.497						−32.734	−39.382			
$TiO_2 + 2HF \rightleftarrows TiOF_2(g) + H_2O$	− 9.104						−20.128	−24.048			
$TiO_2 + 4HF \rightleftarrows TiF_4(g) + 2H_2O$	− 2.93						− 2.433	− 2.288			
$TiO_2 + 4HCl \rightleftarrows TiCl_4 + 2H_2O$	− 6.354						− 8.442	− 9.228			
Vanadium, (Organic)											
$2V + 5/2\ O_2 \rightleftarrows V_2O_5$							93.656				
$2V + 3/2\ O_2 \rightleftarrows V_2O_3$							77.832				
$V_2O_5 + 3H_2 + 4HCl \rightleftarrows 2VCl_2 + 5H_2O$	− 0.816						7.496	10.709			
$V_2O_5 + 2H_2 + 6HCl \rightleftarrows 2VCl_3(g) + 5H_2O$							0.307	3.139			
$V_2O_5 + H_2 + 8HCl \rightleftarrows 2VCl_4 + 5H_2O$	−11.718						−10.906	−11.147			
$V_2O_3 + H_2 + 4HCl \rightleftarrows 2VCl_2 + 3H_2O$	− 9.46						− 7.452	− 6.756			
$V_2O_3 + 6HCl \rightleftarrows 2VCl_3 + 3H_2O$							−15.141	−14.326			
$V_2O_3 + 8HCl \rightleftarrows 2VCl_4(g) + 3H_2O + H_2$	−20.362						−26.354	−27.416			
Ytterbium											

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Table E-2, Part 9. THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF LOG K_{eq} WITH TEMPERATURE

	Temperature, K										
	1300	1200	1100	1000	900	800	700	600	500	400	298
	log K_{eq}										
Zinc, ZnS											
$ZnS + 2O_2 \rightleftarrows ZnSO_4$		16.691					40.42	50.017			
$ZnS + 3/2\ O_2 \rightleftarrows ZnO + SO_2$							29.142				
$ZnS + O_2 \rightleftarrows Zn + SO_2$							8.378				
$ZnS + H_2 \rightleftarrows Zn + H_2S$	− 4.021						−10.666	−12.856			
$ZnS + H_2O \rightleftarrows ZnO + H_2S$	− 2.959						− 5.538	− 6.467			
$ZnS + H_2O + CO_2 \rightleftarrows ZnCO_3 + H_2S$	−30.269						−29.016	−28.742			
$ZnO + CO_2 \rightleftarrows ZnCO_3$	−27.31						−23.478	−22.275			
$ZnS + 2HCl \rightleftarrows ZnCl_2 + H_2S$	− 1.947						− 2.221	− 1.734			
$ZnS + 2HF \rightleftarrows ZnF_2 + H_2S$			− 3.608				− 3.573	− 3.044			
$ZnO + 2HCl \rightleftarrows ZnCl_2 + H_2O$	1.012						3.317	4.733			
$ZnO + 2HF \rightleftarrows ZnF_2 + H_2O$			− 2.745				1.965	3.423			
$Zn + 1/2\ O_2 \rightleftarrows ZnO$							20.764				
$ZnSO_4 + 4H_2 \rightleftarrows ZnS + 4H_2O$		15.039					22.124	24.757			
Zirconium, $ZrSiO_4$											
$ZrO_2 + 4HF \rightleftarrows ZrF_4(g) + 2H_2O$	− 2.393						2.307	4.749			
$ZrO_2 + 4HCl \rightleftarrows ZrCl_4(g) + 2H_2O$	− 7.643						−11.408	−12.807			

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By comparing the equilibrium constants for each element and reaction with the corresponding value of the operating region, the more stable form of the element can be determined. At 700K, the value of log K_{eq} for the reaction —

$$CdS + 3/2\ O_2 \rightleftarrows CdO + SO_2$$

is 26.036. The corresponding operating region value for the pretreater at 700K is −1.14 (see Table E-1). Obviously, cadmium oxide is much more stable under these conditions than cadmium sulfide.

The results of comparing operating region values with the equilibrium values for the elements are summarized in Table E-3. The thermodynamically stable form of cadmium in the pretreater is the sulfate. In general, oxide and sulfate forms are stable in the pretreater, while sulfides and elemental forms are stable in the hydrogasifier and CO-shift reactors.

By combining the thermodynamic data for each element, it is possible to determine what compounds will be favored in each reactor and, hence, to what extent each trace or minor element will be removed from the product gas stream. The solubilities, vapor pressures, and other physical properties were used to evaluate the removal of pollutants downstream from the reactors.

Across the periodic array of elements, the trend is for first-and second-period elements to be stable as carbonates; the elements of periods 3B, 4B, and 5B to be more stable as oxides; and the metals to be more stable as sulfides up through the transition elements. Heavier metals (e.g., mercury, lead, bismuth) tend to exist in elemental form. Hydrides form with members of the carbon, nitrogen, and oxygen families.

It is assumed that the scrub units are highly efficient in particulate removal and that the operating temperature of each unit is relatively uniform. The gas residence time in the light-oil vaporizer is assumed to be sufficient to condense all condensable materials (such as volatilized metals) on the fluidized drying bed. The materials passing overhead from the cyclone to the CO-shift reactor are assumed to be gaseous and contain only small quantities of minute particulates. Some condensable materials may be transported on these entrained particulates.

Table E-3. THERMODYNAMICALLY STABLE FORMS OF ELEMENTS IN THE PROCESS UNITS

Element	Pretreater*	HYGAS*	CO-Shift*
Sb	SA	S	S
As	SA	E, H	E, H
Ba	SA	C	C
Be	O	O	O
Bi	SA	E, S	E, S
B	O	F	F
Cd	SA	S	S
Ca	SA	S	C
Cl	E	HCl	HCl
Cr	SA	S	S
Co	SA	S	S
Cu	SA	S	S
F	E	HF	HF
Ge	O	H	H
Fe	SA	S	S
Pb	SA	S	S
Li	O	C	C
Mg	SA	S	C
Mn	SA	S	S
Hg	E	E, S	E
Mo	SA	S	S
Ni	SA	S	S
N	E, O	H	H
K	O	C	C
Sm	O	O	O
Se	O	H	H
Si	O	O	O
Ag	SA	S, E	E
Na	O	C	C
Sr	SA	C	C
S	O	H	H
Te	O	H	H, E
Sn	O	E, Cl	Cl
Ti	O	O	O
V	O	O	O
Yb	O	O	O
Zn	SA	S	S
Zr	O	O	O

---

* C = carbonate; E = element; H = hydride; O = oxide; S = sulfide; and SA = sulfate.

APPENDIX F. EXAMPLE OF OPERATING-REGION DETERMINATION

The operating regions for the different reactions may be determined from the gas compositions in each reaction unit. These values are calculated in the tables and indicated on each figure where applicable by a labeled circle. The basis for the calculations and concurrent assumptions about operating regions lies in fundamental physical laws. For each reaction, the change in the Gibb's Free Energy value (ΔG) can be related to the equilibrium constant (K_{eq}) by the equation

$$\Delta G = -RT \ln K_{eq}$$

where R is the gas constant, and T is the absolute temperature of the system. The equilibrium constant can be calculated for gas phase reactions by measuring the composition of the gaseous products at the end of a reaction which began with known quantities of reactants. This type of test and analysis has been done on a large number of reactions, the results of which are tabulated and published in numerous references.[5,17,21-23,26,27,38,42,61,63,64]

For a typical gas phase reaction the equilibrium constant can be written:

$$K_{eq} = \frac{[P_C]^c \, [P_D]^d}{[P_A]^a \, [P_B]^b}$$

where the bracketed quantity represents the partial pressure (in atmospheres) of the products or reactants at equilibrium. Each quantity is raised to the power of its stoichiometric coefficient.

Equilibrium constants of heterogeneous gas reactions (gas-solid, gas-liquid) are somewhat more complex than gas-phase reactions requiring the additional concept of activity. The equilibrium constant for the reaction

$MS(s) + H_2O(g) \rightleftarrows MO(s) + H_2S(g)$, takes the form:

$$K_{eq} = \frac{[aMO][P_{H_2S}]}{[aMS][P_{H_2O}]}$$

where "a" is the activity of the solid phase component. Solid phase activities are usually assumed to be near unity to expedite calculations, hence, the equilibrium constant can be determined from the partial pressures of H_2S and H_2O in the reaction vessel at equilibrium. If the vapor pressure of the solid or liquid components is calculable at the reaction temperature, the partial pressure should be used in the calculation of K_{eq}.

In this study, the mole percentages of the gaseous components in the main reactors are assumed to be constant during steady-state operation. Thus, in the hydrogasifier, the value of $[P_{H_2S}] / [P_{H_2O}]$ is a constant. Since K_{eq} is known from previous calculations, the ratio of products (solid) to reactants (solid) can be determined directly. This provides the thermodynamically favored form of the element for that reaction in that reactor unit. The concept of operating regions is derived from this treatment.

The operating region for the reactions of Figure E-1 may be calculated from the mole fraction data of Table 1, Part 3, Column D (pretreater off-gases). The operating region at 700K may be calculated as log $[1/(P_{O_2})^{3/2}]$, which follows from the form of K_{eq} for these reactions:

$$K_{eq} = \frac{[aMSO_3]}{[aMS]\ [P_{O_2}]^{3/2}}$$

In this case, $P_{O_2} = 0.21$ atm and log $[1/(P_{O_2})^{3/2}] = 1.02$. The K_{eq} values are much higher than 1.02 in these reactions, and the thermodynamic driving force tends strongly to the right, favoring oxidation to sulfites. Had the operating region been greater than the K_{eq} values, the driving force would have been to the left, favoring reduction to sulfides.

The assumption that the mole fraction of a component in a gas is equal to its partial pressure is supported in the following discussion.

Partial-Pressure Calculations

The Ideal Gas Law states that the mole fraction of a gas is directly proportional to its partial pressure:

$$\frac{P_i}{P_T} = \frac{n_i}{\Sigma n_i} = X_i$$

At low pressures and high temperatures one may readily calculate the partial pressure of a component in a gaseous mixture. This law was applied to the gases in the HYGAS reactors to estimate the partial pressures needed to calculate the operating regions for the different reactions.

Calculations were based on 100 atm pressure in the hydrogasifier and CO-shift reactor. Thus, the mole percent of a gas in the hydrogasifier was numerically equal to its partial pressure: e.g., for H_2O, 17.81 mol % indicates a partial pressure of 17.81 atm. Since the HYGAS process is designed to operate at pressures ranging from 70 to 100 atmospheres, 100 atm was chosen over a median value for convenience. Pretreater calculations were based on 1 atm pressure.

The validity of the Ideal Gas Law at these conditions was checked by calculating the reduced pressure and temperature for each process gas and determining the compressibility factor (Z) and fugacity coefficients (f/p) from generalized tables. The values of Z and f/p are listed below. Because the values are all very near 1.0, the assumption holds.

	T_c	P_c	T_r*	P_r†	Z	f/p
CO	134.15	35	8.94	2.57	0.997	1.002
CO_2	304.25	73	3.9	1.2	1.000	1.000
H_2	34.25	12.8	35.04	7.03	1.09	1.09‡
H_2O	647.3	218.4	1.85	0.412	0.989	0.984
CH_4	190.65	45.8	6.29	1.97	0.996	1.000
H_2S	373.55	88.9	3.2	1.01	1.000	1.000

* $T_r = 1200K/T_c$.

† $P_r = 90\ atm/P_c$.

‡ Each table listed T_r maximum as 15.00. T_r for hydrogen here is 35.04.

APPENDIX G. BASIS FOR CALCULATIONS

The objective of the present study is to prepare an environmental test plan to investigate the fate of constituents of coal and potential pollutants during coal gasification. The basis for this test plan is the analytical data acquired from four series of gasification runs in a 0.1 m diameter reactor of the HYGAS process development unit. The operating conditions of these runs were 1160K (1630 °F) and 6935 kN/m^2 (1006 psia). The gasification runs did not include a steam-oxygen gasifier, nor were there any gaseous or liquid samples tested, since the gasification runs were conducted a few years prior to this program. The net carbon gasified in these runs was about 40%.

Some comments should be made on the applicability of these test data and operating conditions to a commercial design. First, one may expect more extreme conditions to be experienced in a commercial plant. The steam-oxygen gasifier will produce much higher temperatures than the present tests have reached and will cause more materials to be volatilized. Indeed, the amount of carbon gasified should exceed 90% of the original coal feed. Second, a commercial plant will most likely operate at higher pressures than these bench-scale tests. This will allow for pressure drops across the system to supply product gas at a nominal 6995 kN/m^2 (1015 psia) rate without the need for additional compression. Third, the coal-feed and ash-discharge systems are quite different. The bench-scale reactor is dry-fed and dry-discharged; the commercial plant will incorporate a slurry feed system using either a light oil or water as the slurry medium. Ash material will be slurried and discharged in a similar manner.

The slurry medium presents another sink for the soluble trace-elements which may tend to accumulate with time. This factor is not encountered in the bench-scale tests and may prove to be a significant part of the total potential pollutants to be carefully studied.

The differences between the bench-scale reactor runs and a commercial plant operation are many, and yet the data derived from the former may with justification be scaled-up to the latter. First, we must be cognizant of the differences between the PDU and the commercial plant and of how they affect the actual operations. Second, the thermodynamic differences, as they relate to trace-element volatilization and reactions, must be considered with the process changes. Third, the information gathered from analyses of the bench-scale gasification runs is the most complete look available at the fate of trace elements during hydrogasification. The importance of gathering additional data in a comprehensive program to evaluate the environmental impact of coal-gasification processes cannot be overemphasized. Our current work indicates that the purification units connected with a HYGAS plant will eliminate the toxic trace-elements, but further assurances are required for the private as well as public acceptance of a new energy source.